

## **Supporting Information**

### **Neptunyl peroxide chemistry: synthesis and spectroscopic characterization of a neptunyl triperoxide compound, $\text{Ca}_2[\text{NpO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$**

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## I. Supporting experimental results

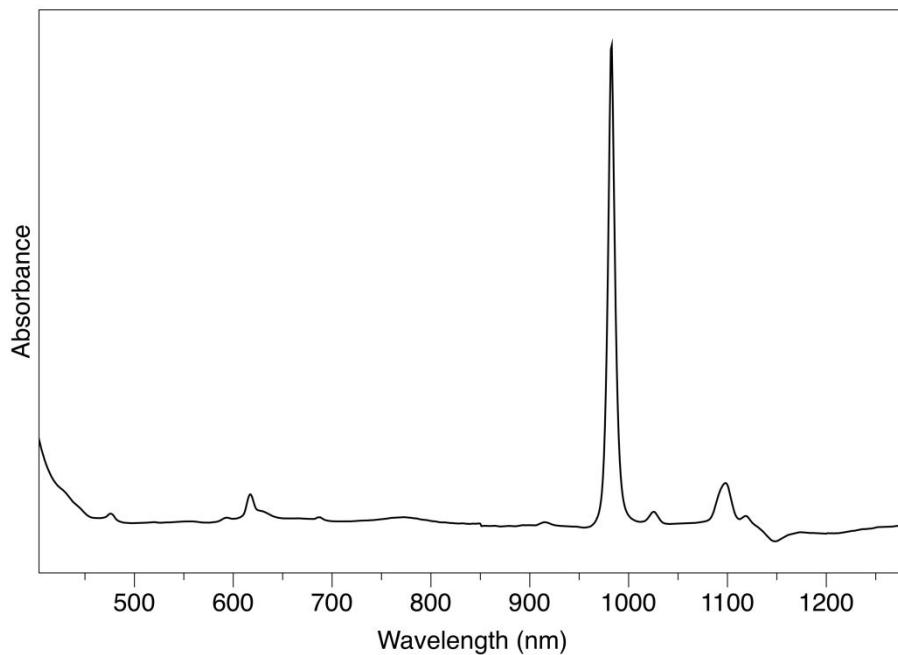
### Bond Valence Calculations

$$\text{Valence contribution, } S = e^{[(R_o - R)/B]}$$

R = observed bond length, Np(V):  $R_o = 2.036$ , B = 0.411<sup>1</sup>, Np(VI):  $R_o = 2.022$ , B = 0.0523<sup>1</sup>

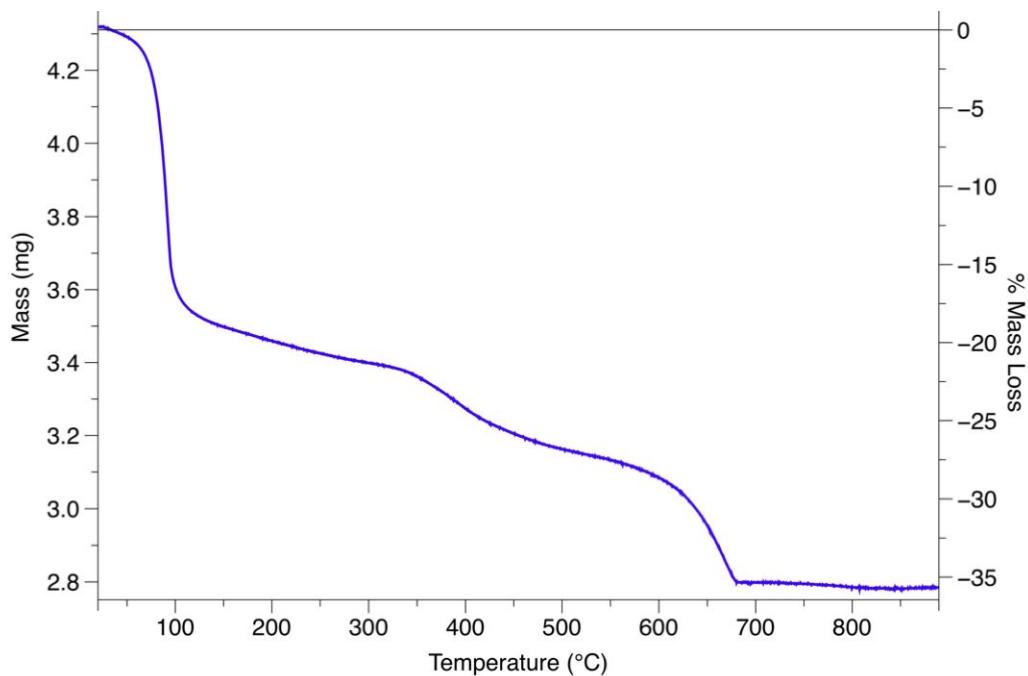
	Bond length	S, Np(V)	S, Np(VI)
<b>Np1-O1</b>	1.843	1.599	1.408
<b>Np1-O1</b>	1.843	1.599	1.408
<b>Np1-O2</b>	2.290	0.555	0.599
<b>Np1-O2</b>	2.290	0.555	0.599
<b>Np1-O3</b>	2.286	0.544	0.604
<b>Np1-O3</b>	2.286	0.544	0.604
<b>Np1-O4</b>	2.278	0.538	0.613
<b>Np1-O4</b>	2.278	0.538	0.613
<b>Valence Sum</b>	<b>6.473</b>	<b>6.446</b>	

**Figure S1.** UV-vis-NIR spectrum of ~0.1 M Np(V) in 1 M HCl stock solution acquired with a Jasco V-670 spectrophotometer.

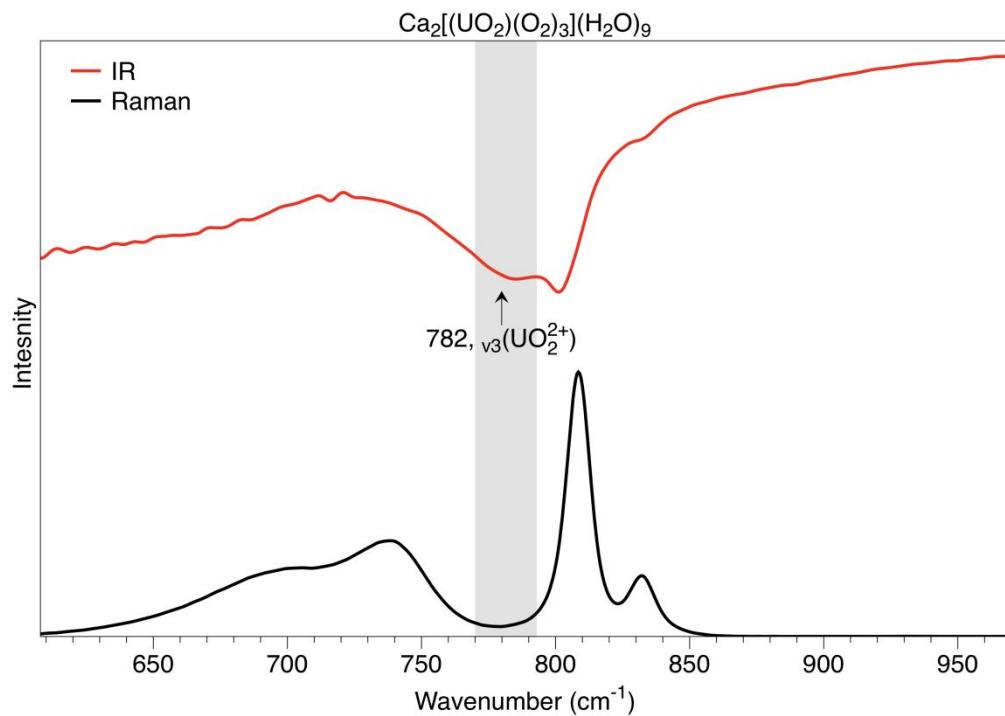


(1) Gagné, O. C.; Hawthorne, F. C., Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Cryst. B* **2015**, *71* (5), 562-578.

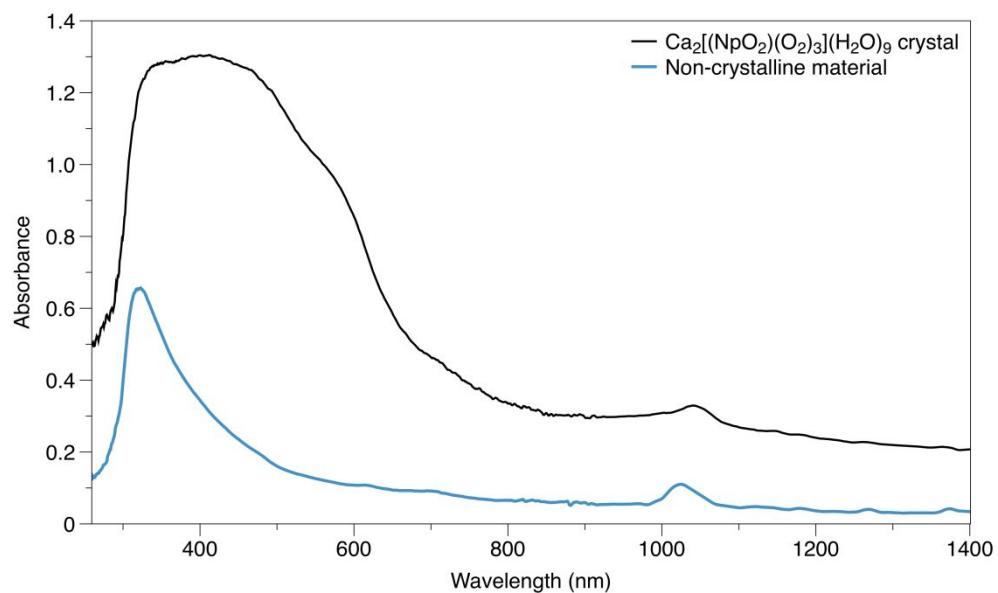
**Figure S2.** Thermogravimetric analysis of crystals of  $\text{Ca}_2[\text{NpO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$ .



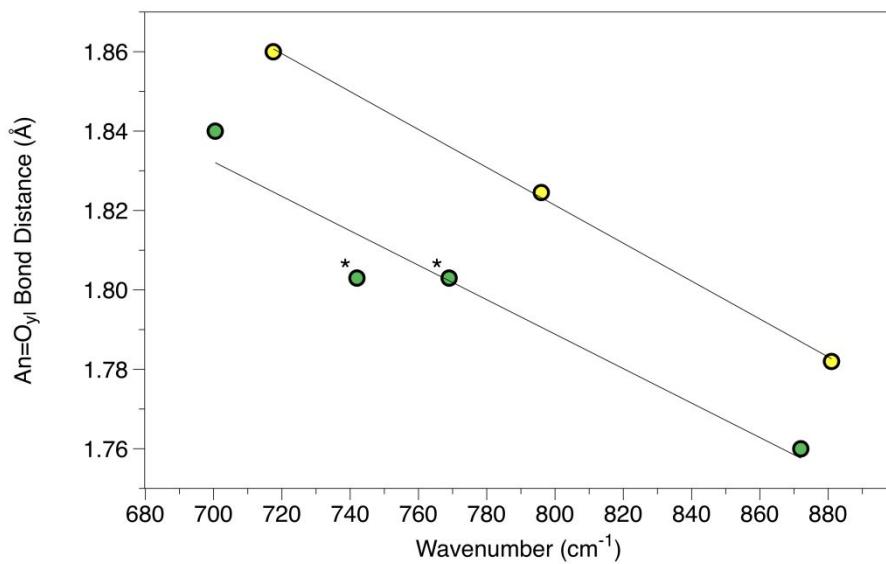
**Figure S3.** Experimental IR and Raman spectra of  $\text{Ca}_2[\text{UO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$ , showing the asymmetric uranyl mode in the IR spectrum.



**Figure S4.** UV-vis-NIR spectra of  $\text{Ca}_2[\text{NpO}_2(\text{O}_2)_3]\cdot 9\text{H}_2\text{O}$  (**1**) crystals and a possible impurity collected using a Craic Technologies UV-vis-NIR spectrophotometer. The spectra of **1** display broad features, including signals between 450 and 650 nm that may arise from charge transfer bands typical of Np(VI). A broad, weak signal at 1030 nm might be attributed to 5f–5f transitions, but this signal falls between the usual wavelengths of 980 and 1200 nm for Np(V) and Np(VI), respectively, and occurs in a non-crystalline impurity.<sup>2,3</sup>



**Figure S5.** A plot of neptunyl and uranyl vibrational modes for isostructural compounds. The asterisks represent the neptunyl compound  $[\text{Co}(\text{NH}_3)_6]_2[\text{NpO}_2(\text{OH})_4]_3 \cdot \text{H}_2\text{O}$  that sometimes has two observed signals.



(2) Hagan, P. G.; Cleveland, J. M., The absorption spectra of neptunium ions in perchloric acid solution. *J. Inorg. Nucl. Chem.* **1966**, *28* (12), 2905–2909.

(3) Reed, D. T.; Matsika, S.; Pitzer, R. M. Intensities in the spectra of actinyl ions. *J. Phys. Chem. A* **2000**, *104* (51).

## II. Computational results

**Table S1.** Relative stability (in kj/mol) of six different models of  $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution. \* Optimized Model-III structure with M06L has two negative frequencies around  $-90 \text{ cm}^{-1}$  and  $-41 \text{ cm}^{-1}$ . We were unable to remove these two negative frequencies only for this structure.

$\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$	PBE	PBEO	B3LYP	M06L
Model-I	10.2	13.4	0	16.1
Model-II	57.4	59.3	50.7	47.9
Model-III	3.3	0	19.0	0*
Model-IV	37.7	35.9	26.8	31.5
Model-V	0	4.8	15.3	0.3
Model-VI	21.1	21.1	11.9	17.5

**Table S2.** Average distances in Å and angles in degrees from the most energetically favorable optimized geometries of  $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

Model	Functional	$\text{Np-O}_{\text{yl}}$	$\text{Np-O}_{\text{eq}}$	$\text{O}_{\text{eq}}-\text{O}_{\text{eq}}$	$\text{Ca}^{2+}-\text{O}_{\text{eq}}$	$\text{Ca}^{2+}-\text{O}_{\text{yl}}$	$\text{O}_{\text{yl}}-\text{Np-O}_{\text{yl}}$
Model I	PBE	1.920	2.346	1.467	2.374	2.460	172.1
	PBEO	1.846	2.323	1.445	2.368	2.562	175.9
	M06-L	1.890	2.361	1.463	2.365	2.498	172.6
	B3LYP	1.877	2.359	1.470	2.375	2.549	174.1
Model II	PBE	1.869	2.355	1.481	2.292	4.798	178.1
	PBEO	1.817	2.325	1.458	2.286	4.754	178.8
	M06-L	1.841	2.372	1.476	2.296	4.810	178.5
	B3LYP	1.844	2.356	1.483	2.300	4.794	177.9
Model III	PBE	1.910	2.343	1.467	2.332	2.439	176.3
	PBEO	1.844	2.309	1.447	2.314	2.471	177.4
	M06-L	1.892	2.361	1.459	2.339	2.451	176.2
	B3LYP	1.883	2.344	1.472	2.347	2.498	175.7
Model IV	PBE	1.901	2.360	1.454	2.380	2.887	177.7
	PBEO	1.829	2.328	1.434	2.380	2.939	178.1
	M06-L	1.874	2.377	1.447	2.382	2.882	177.4
	B3LYP	1.860	2.362	1.459	2.392	2.946	177.8
Model V	PBE	1.913	2.335	1.469	2.332	2.421	174.8
	PBEO	1.844	2.304	1.448	2.324	2.458	176.8
	M06-L	1.886	2.349	1.463	2.331	2.439	175.0
	B3LYP	1.887	2.338	1.474	2.352	2.512	174.9
Model VI	PBE	1.917	2.345	1.460	2.387	2.543	178.7
	PBEO	1.846	2.314	1.439	2.379	2.577	179.5
	M06-L	1.890	2.363	1.453	2.385	2.548	178.2
	B3LYP	1.879	2.350	1.463	2.404	2.604	179.7
Avg. expt. Value (this work)		1.842(7)	2.285(5)	1.505(8)	2.452(38)	2.650(7)	177.2(4)

**Table S3.** Assignment of Raman spectra (in  $\text{cm}^{-1}$ ) of six different models of  $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

Model	Functional	$\nu_1(\text{NpO}_2^{2+})$	$\nu_3(\text{NpO}_2^{2+})$	$\nu_1(\text{O}_2^{2-})$	$\nu_2(\text{O}_2^{2-})$	$\nu_3(\text{O}_2^{2-})$
Model I	PBE	584	611	895	816	820
	PBEO	672	712	962	912	907
	M06-L	597	639	884	793	789
	B3LYP	636	673	908	848	842
Model II	PBE	626	665	879	823	829
	PBEO	729	770	934	913	910
	M06-L	639	689	868	798	802
	B3LYP	681	725	881	859	854
Model III	PBE	539	655	892	841	843
	PBEO	636	750	956	913	919
	M06-L	527	659	882	823	824
	B3LYP	604	726	891	855	862
Model IV	PBE	582	634	916	860	870
	PBEO	668	723	985	932	948
	M06-L	572	640	918	854	865
	B3LYP	618	678	928	870	886
Model V	PBE	597	636	885	834	838
	PBEO	672	714	949	939	915
	M06-L	600	656	875	810	819
	B3LYP	637	685	885	859	852
Model VI	PBE	567	664	899	851	849
	PBEO	632	738	974	935	920
	M06-L	562	664	899	840	834
	B3LYP	601	707	916	867	873
Expt. Value (this work)		683, 718	-	834	808	-

**Table S4.** Relative stability (in kj/mol) of six different models of  $\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

<b><math>\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]</math></b>	<b>PBE</b>	<b>PBEO</b>	<b>B3LYP</b>	<b>M06L</b>
Model-I	14.0	15.9	13.0	14.3
Model-II	57.5	40.7	40.0	47.4
Model-III	6.9	4.8	5.7	4.9
Model-IV	47.0	53.0	50.5	46.8
Model-V	0	0	0	0
Model-VI	32.5	26.3	26.8	29.5

**Table S5.** Average distances in Å and angles in degrees from the most energetically favorable optimized geometries of  $\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

<b>Model</b>	<b>Functional</b>	<b><math>\text{U}-\text{O}_{\text{yl}}</math></b>	<b><math>\text{U}-\text{O}_{\text{eq}}</math></b>	<b><math>\text{O}_{\text{eq}}-\text{O}_{\text{eq}}</math></b>	<b><math>\text{Ca}^{2+}-\text{O}_{\text{eq}}</math></b>	<b><math>\text{Ca}^{2+}-\text{O}_{\text{yl}}</math></b>	<b><math>\text{O}_{\text{yl}}-\text{U}-\text{O}_{\text{yl}}</math></b>
Model I	PBE	1.947	2.310	1.476	2.431	2.375	168.8
	PBEO	1.886	2.285	1.451	2.389	2.431	169.3
	M06-L	1.920	2.324	1.468	2.391	2.418	167.3
	B3LYP	1.911	2.316	1.474	2.408	2.450	168.8
Model II	PBE	1.893	2.335	1.486	2.304	4.800	178.4
	PBEO	1.840	2.311	1.460	2.298	4.759	178.4
	M06-L	1.869	2.350	1.480	2.308	4.810	178.4
	B3LYP	1.865	2.339	1.485	2.313	4.803	178.4
Model III	PBE	1.936	2.312	1.476	2.348	2.411	175.6
	PBEO	1.874	2.288	1.452	2.330	2.463	175.6
	M06-L	1.908	2.328	1.470	2.345	2.430	175.5
	B3LYP	1.901	2.317	1.476	2.359	2.478	175.5
Model IV	PBE	1.942	2.305	1.463	2.474	2.428	173.1
	PBEO	1.849	2.309	1.442	2.418	3.118	178.8
	M06-L	1.908	2.328	1.455	2.445	2.486	172.9
	B3LYP	1.874	2.337	1.467	2.447	3.136	178.6
Model V	PBE	1.937	2.306	1.476	2.358	2.386	174.3
	PBEO	1.876	2.285	1.451	2.340	2.425	175.4
	M06-L	1.907	2.323	1.469	2.353	2.417	174.6
	B3LYP	1.902	2.312	1.475	2.366	2.433	175.0
Model VI	PBE	1.921	2.319	1.473	2.399	2.745	176.2
	PBEO	1.859	2.298	1.447	2.358	2.829	176.6
	M06-L	1.893	2.336	1.467	2.396	2.769	176.3
	B3LYP	1.886	2.326	1.473	2.402	2.785	176.3
Avg. expt. value (previously reported) <sup>1</sup>		1.840(7)	2.297(14)	1.507(21)	2.457(43)	2.701(7)	177.0

<sup>1</sup> Kubatko, K. A.; Forbes, T. Z.; Klingensmith, A. L.; Burns, P. C., Expanding the crystal chemistry of uranyl peroxides: synthesis and structures of di- and triperoxodioxouranium(VI) complexes. *Inorganic Chemistry* **2007**, 46, 3657-3662.

**Table S6.** Assignment of Raman spectra (in  $\text{cm}^{-1}$ ) of six different models of  $\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

Model	Functional	$v_1(\text{UO}_2^{2+})$	$v_3(\text{UO}_2^{2+})$	$v_1(\text{O}_2^{2-})$	$v_2(\text{O}_2^{2-})$	$v_3(\text{O}_2^{2-})$
Model I	PBE	598	600	876	833	838
	PBEO	672	675	948	914	924
	M06-L	595	613	865	815	820
	B3LYP	639	644	895	859	868
Model II	PBE	656	680	860	825	826
	PBEO	726	744	933	911	910
	M06-L	659	691	845	804	805
	B3LYP	695	718	880	857	854
Model III	PBE	565	664	871	835	837
	PBEO	620	738	945	921	917
	M06-L	557	668	858	815	816
	B3LYP	590	707	891	865	860
Model IV	PBE	596	604	899	859	858
	PBEO	697	714	972	935	943
	M06-L	596	617	897	849	851
	B3LYP	666	687	911	869	880
Model V	PBE	603	609	876	838	839
	PBEO	679	686	948	922	920
	M06-L	609	626	864	818	820
	B3LYP	646	655	895	865	864
Model VI	PBE	590	656	884	844	833
	PBEO	665	728	966	938	918
	M06-L	599	666	870	827	811
	B3LYP	633	700	903	872	861
Expt. Value (Previously Reported) <sup>2</sup>		696, 739	782	832	809	-

<sup>2</sup> Dembowski, M.; Bernales, V.; Qiu, J.; Hickam, S.; Gaspar, G.; Gagliardi, L.; Burns, P. C., Computationally-guided assignment of unexpected signals in the Raman spectra of uranyl triperoxide complexes. *Inorganic Chemistry* **2017**, 56 (3), 1574-1580.

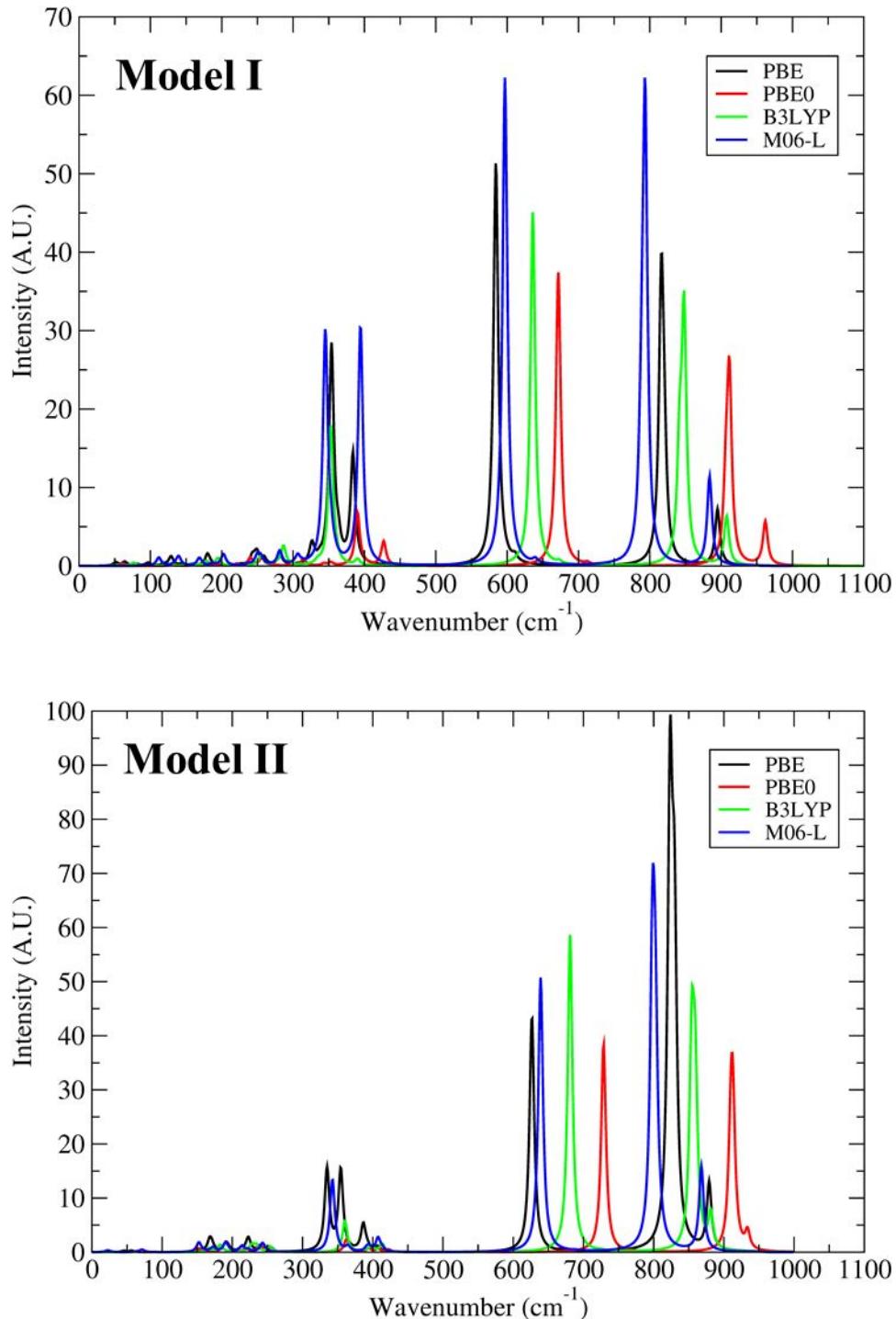
**Table S7.** Comparison of  $v_1(\text{MO}_2^{2+})$  and  $v_1(\text{O}_2^{2-})$  Raman peak (in  $\text{cm}^{-1}$ ) of six different models of  $\text{Ca}_2[\text{M(VI)}\text{O}_2(\text{O}_2)_3]$  at different levels of theory in aqueous solution.

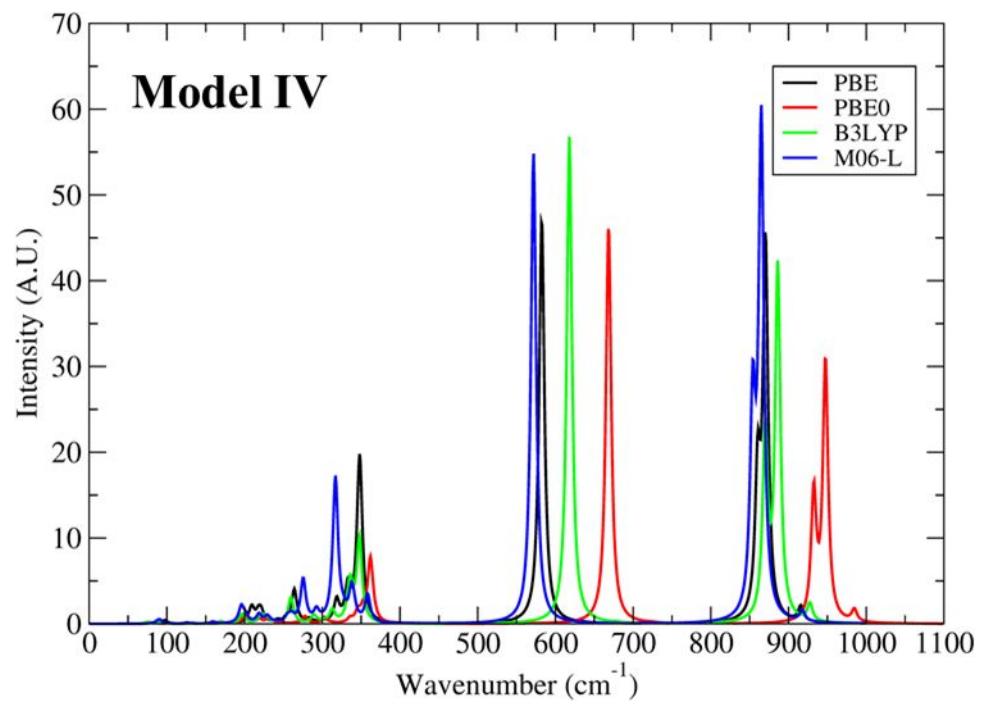
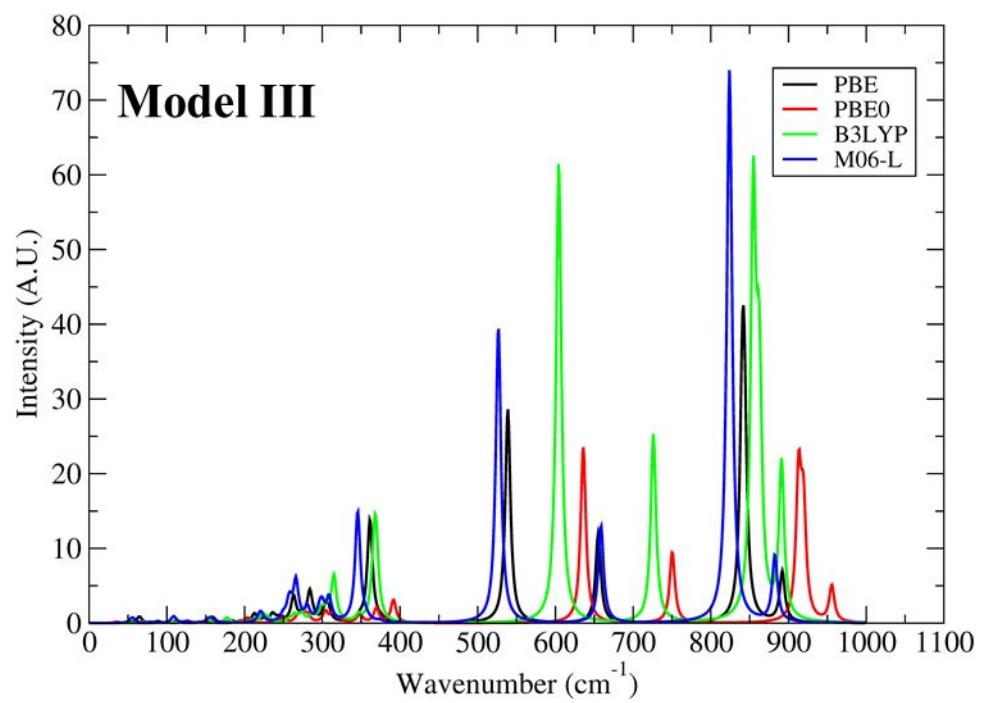
<b>Model</b>	<b>Functional</b>	$v_1(\text{NpO}_2^{2+})$	$v_1(\text{UO}_2^{2+})$	$v_1(\text{O}_2^{2-}) (\text{Np})$	$v_1(\text{O}_2^{2-}) (\text{U})$
Model I	PBE	584	598	895	876
	PBEO	672	672	962	948
	M06-L	597	595	884	865
	B3LYP	636	639	908	895
Model II	PBE	626	656	879	860
	PBEO	729	726	934	933
	M06-L	639	659	868	845
	B3LYP	681	695	881	880
Model III	PBE	539	565	892	871
	PBEO	636	620	956	945
	M06-L	527	557	882	858
	B3LYP	604	590	891	891
Model IV	PBE	582	596	916	899
	PBEO	668	697	985	972
	M06-L	572	596	918	897
	B3LYP	618	666	928	911
Model V	PBE	597	603	885	876
	PBEO	672	679	949	948
	M06-L	600	609	875	864
	B3LYP	637	646	885	895
Model VI	PBE	567	590	899	884
	PBEO	632	665	974	966
	M06-L	562	599	899	870
	B3LYP	601	633	916	903
Expt. Value (this work)		683, 718	696, 739	834	832

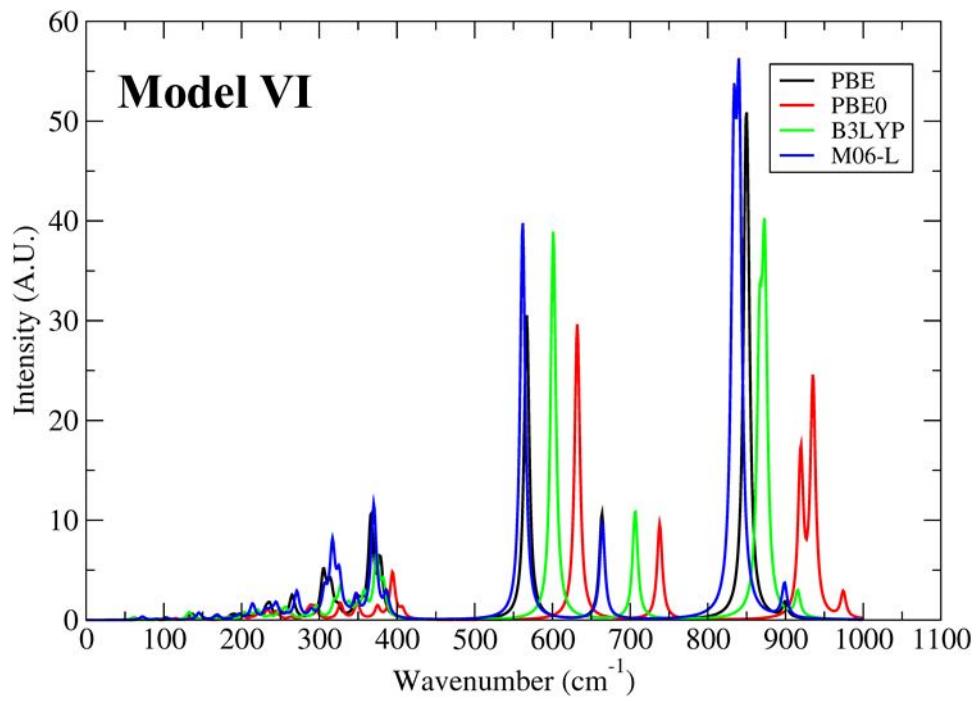
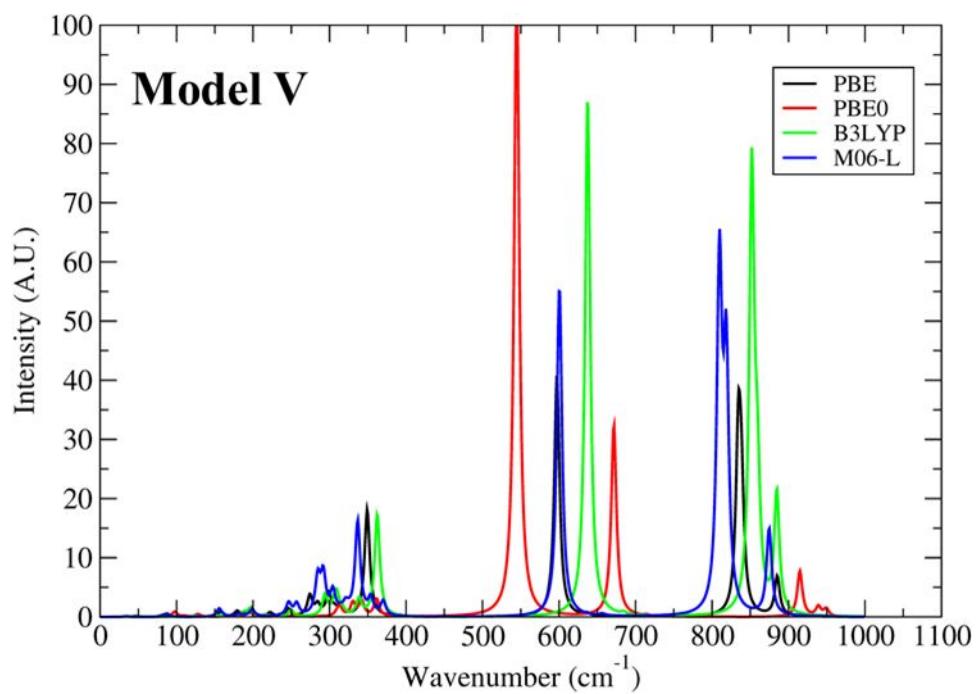
**Table S8.** Average distances in Å and angles in degrees from the most energetically favorable optimized geometries of  $\text{Ca}_2[\text{Np}(\text{V})\text{O}_2(\text{O}_2)_3]^-$  at different levels of theory in aqueous solution.

Model	Functional	$\text{Np-O}_{\text{yl}}$	$\text{Np-O}_{\text{eq}}$	$\text{O}_{\text{eq}}-\text{O}_{\text{eq}}$	$\text{Ca}^{2+}-\text{O}_{\text{eq}}$	$\text{Ca}^{2+}-\text{O}_{\text{yl}}$	$\text{O}_{\text{yl}}-\text{Np-O}_{\text{yl}}$
Model I	PBE	2.018	2.382	1.497	2.374	2.321	169.3
	PBEO	1.976	2.364	1.467	2.350	2.338	167.6
	M06-L	1.998	2.399	1.494	2.370	2.360	169.5
	B3LYP	1.997	2.428	1.496	2.352	2.360	166.4
Model II	PBE	2.002	2.390	1.498	2.313	2.326	173.7
	PBEO	1.955	2.364	1.469	2.303	2.347	172.5
	M06-L	1.971	2.417	1.499	2.313	2.365	175.0
	B3LYP	1.975	2.419	1.498	2.326	2.385	174.1
Model III	PBE	2.005	2.398	1.497	2.308	2.365	175.0
	PBEO						
	M06-L	1.974	2.422	1.498	2.311	2.392	176.2
	B3LYP	1.977	2.419	1.497	2.320	2.394	176.2
Model IV	PBE	2.001	2.388	1.487	2.419	2.338	172.8
	PBEO	1.938	2.369	1.461	2.406	2.377	173.3
	M06-L	1.957	2.445	1.489	2.413	2.504	171.2
	B3LYP	1.967	2.413	1.488	2.481	2.429	173.5
Model V	PBE	1.996	2.392	1.498	2.322	2.333	174.8
	PBEO	1.953	2.364	1.469	2.302	2.347	172.5
	M06-L	1.976	2.411	1.494	2.328	2.368	175.4
	B3LYP	1.975	2.419	1.497	2.326	2.385	174.1
Model VI	PBE	2.004	2.392	1.494	2.371	2.353	178.4
	PBEO	1.947	2.371	1.465	2.348	2.363	178.6
	M06-L	1.973	2.418	1.494	2.370	2.391	178.8
	B3LYP	1.973	2.415	1.494	2.381	2.393	178.8
Avg. expt. Value (this work)		1.842(7)	2.285(5)	1.505(8)	2.452(38)	2.650(7)	177.2(4)

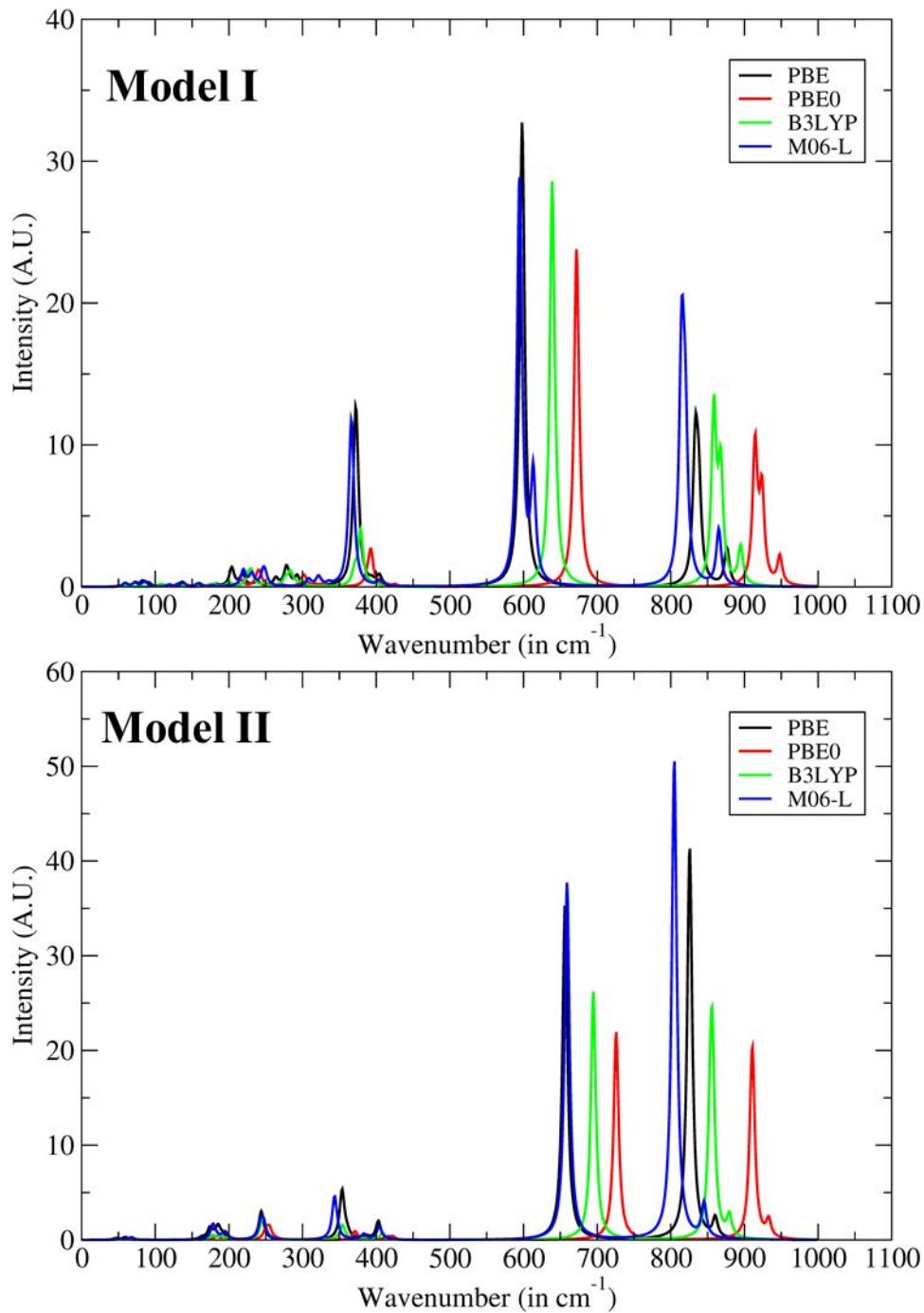
**Figure S6.** Computed Raman spectra of Models I – VI of  $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$  using different levels of theory in aqueous solution.

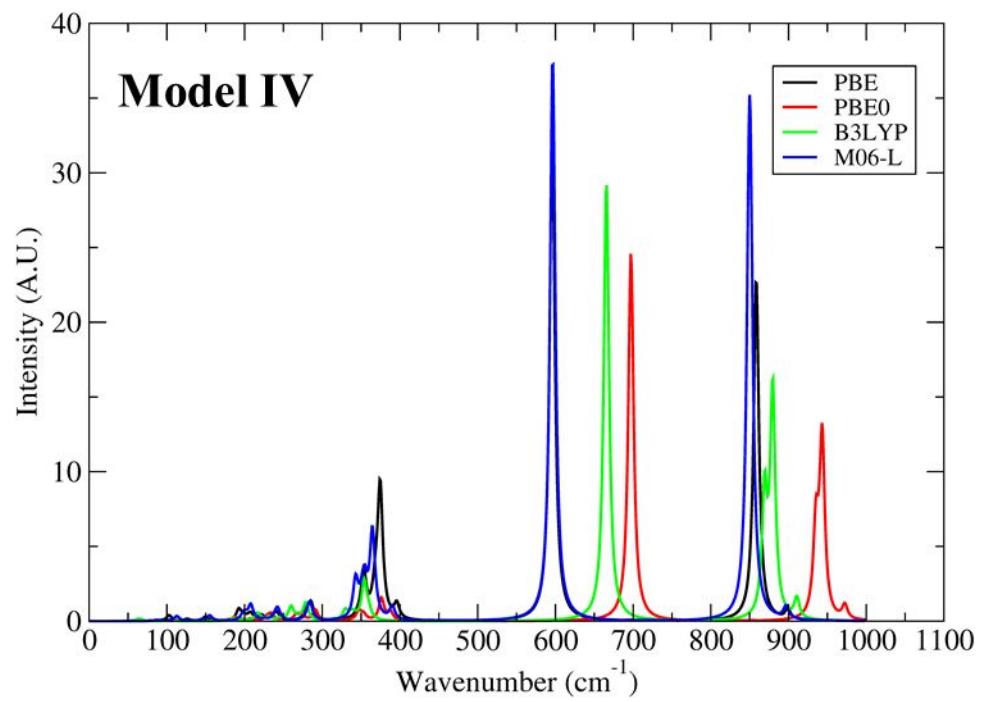
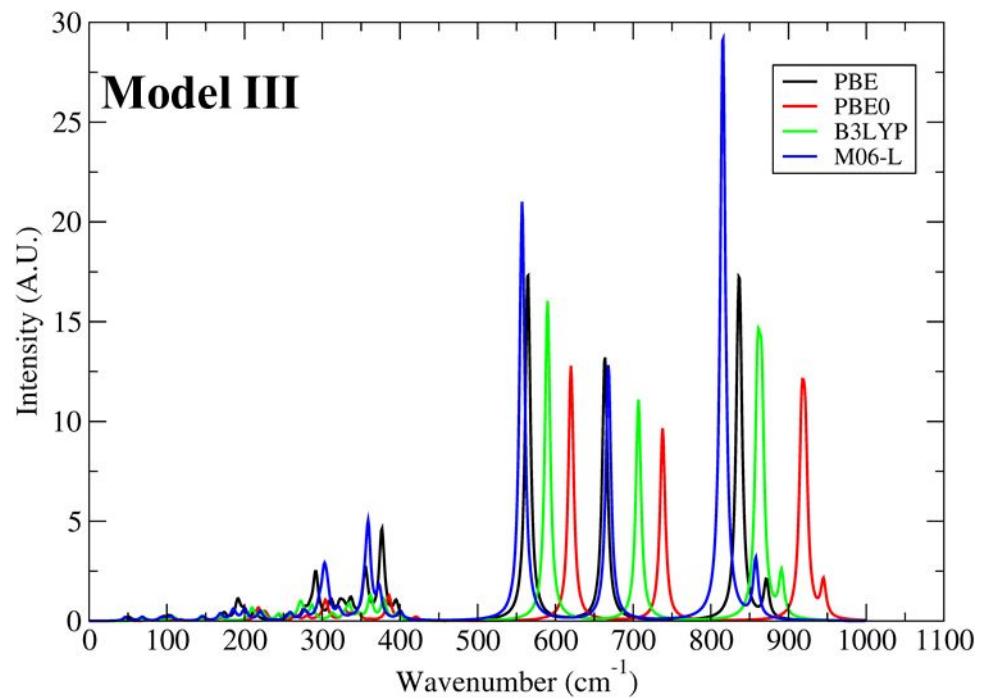


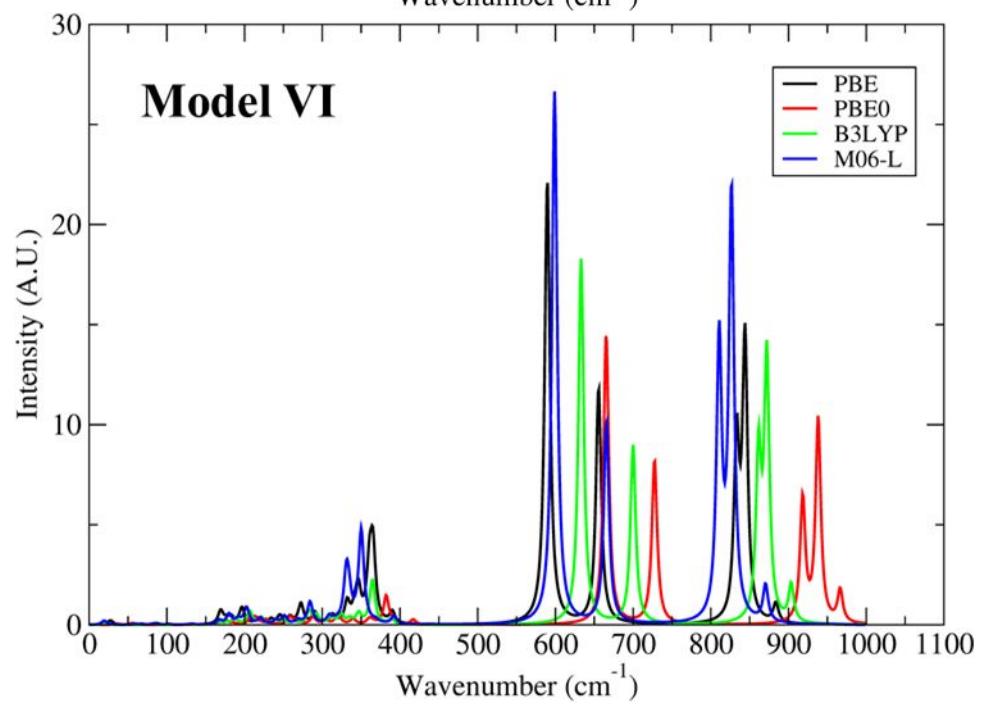
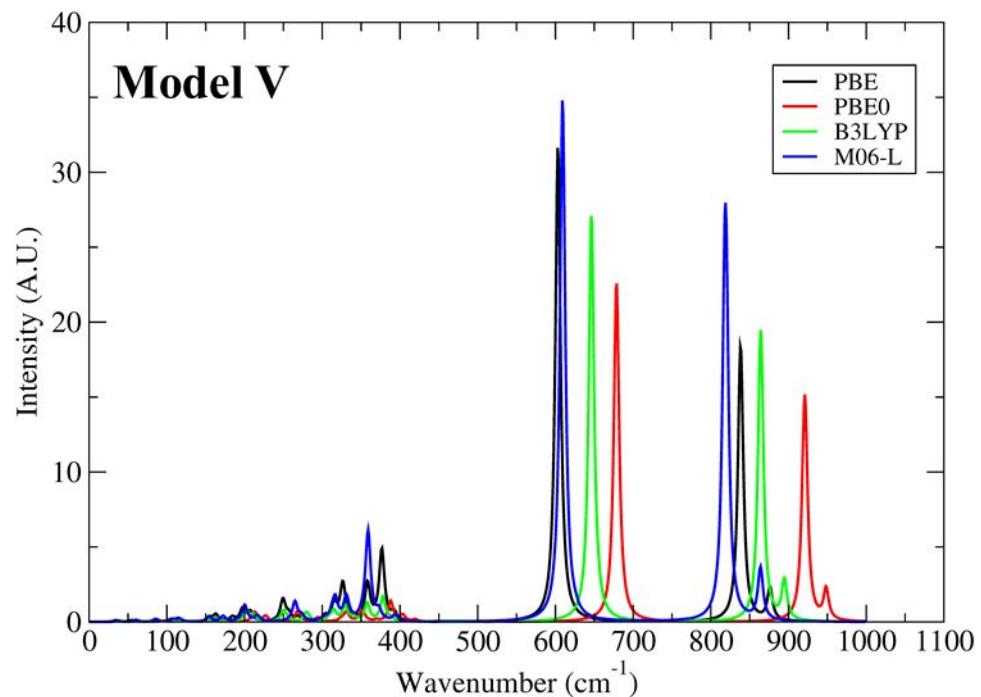




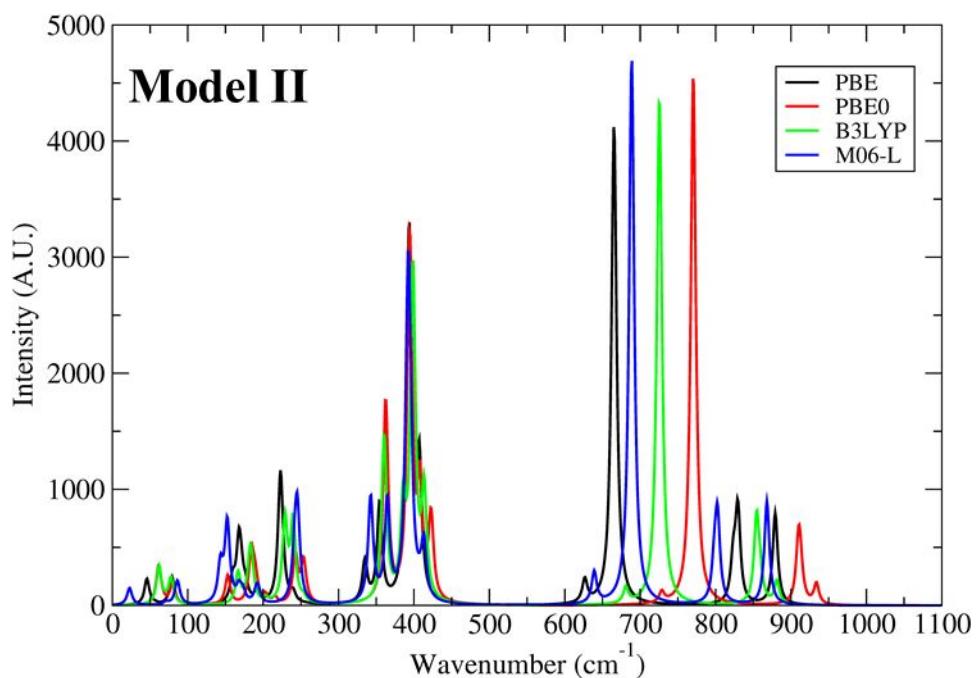
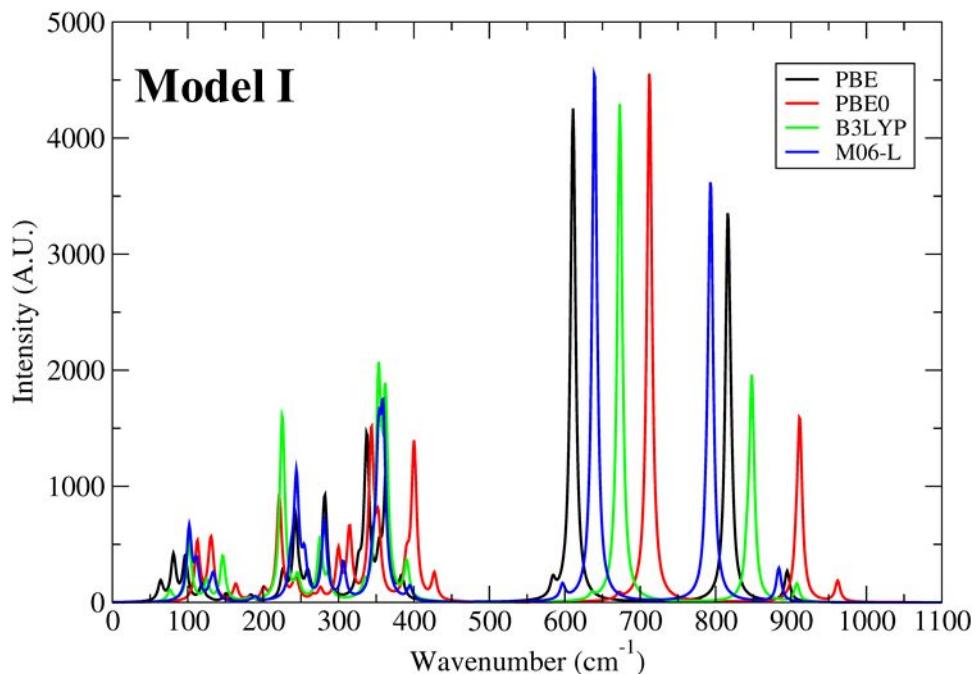
**Figure S7.** Computed Raman spectra of Model I – VI of  $\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$  using different levels of theory in aqueous solution.

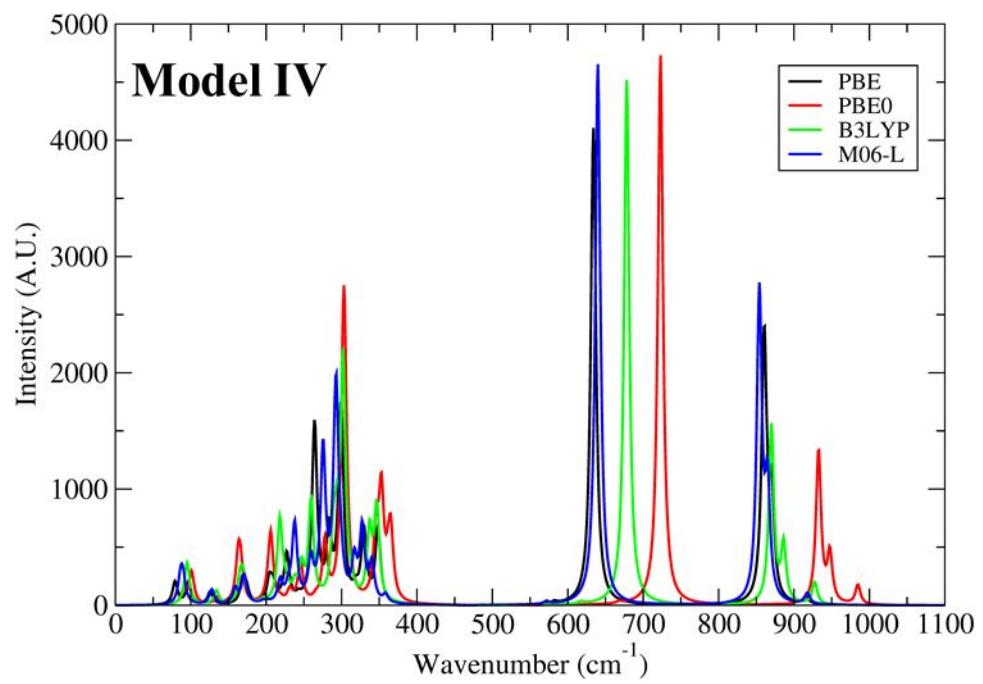
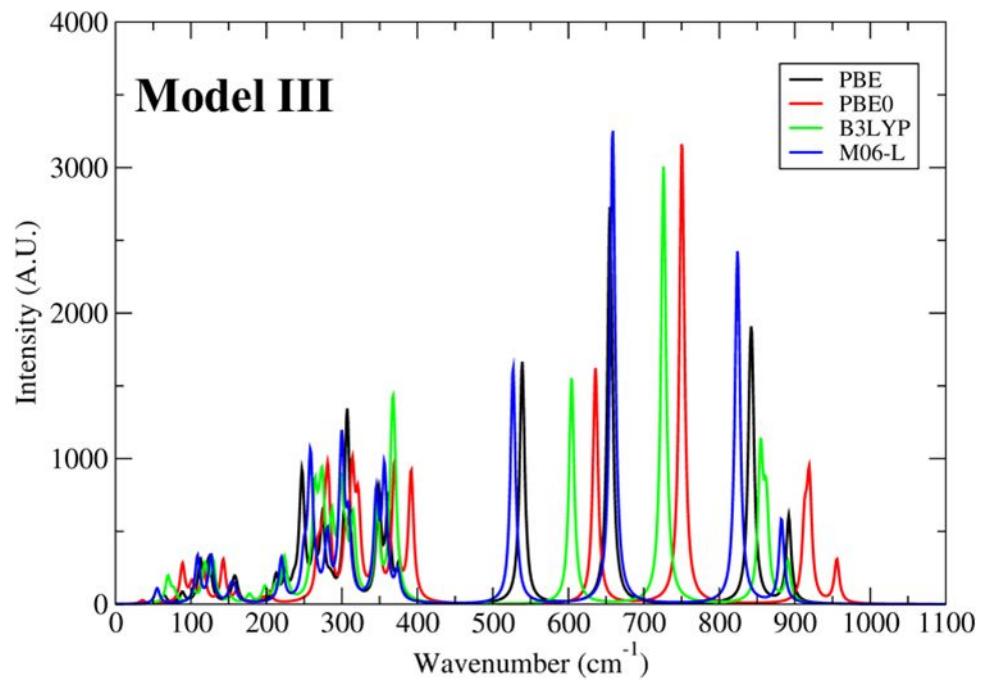


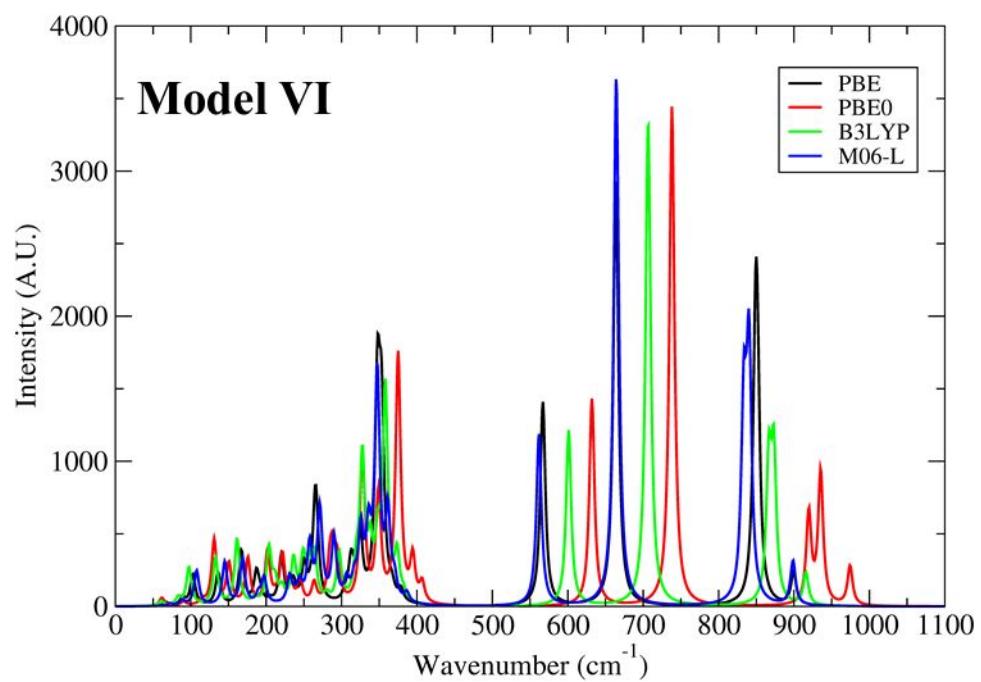
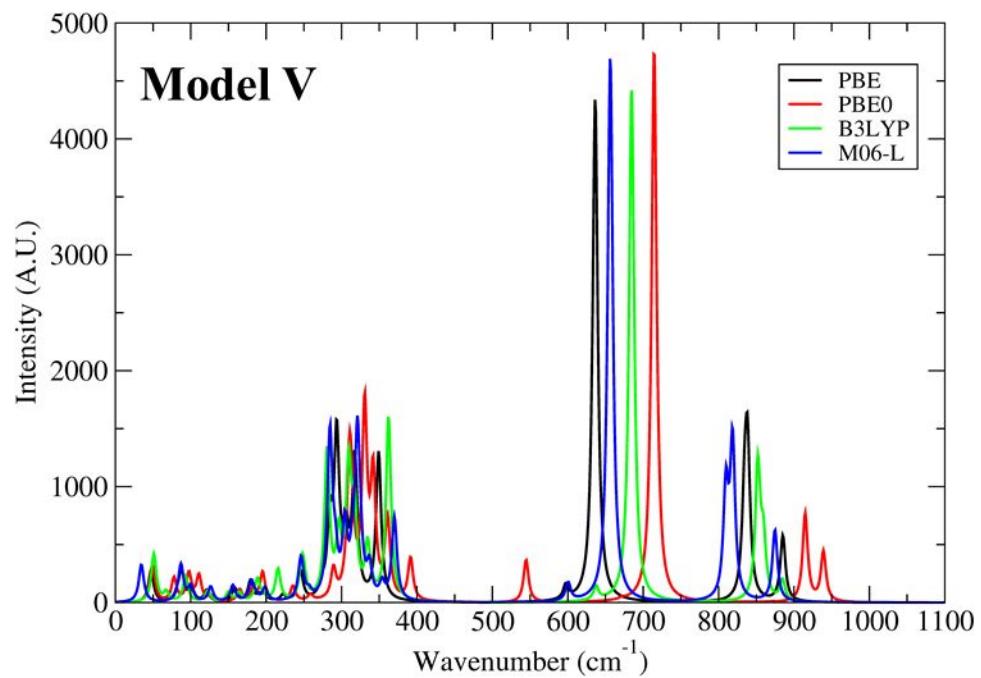




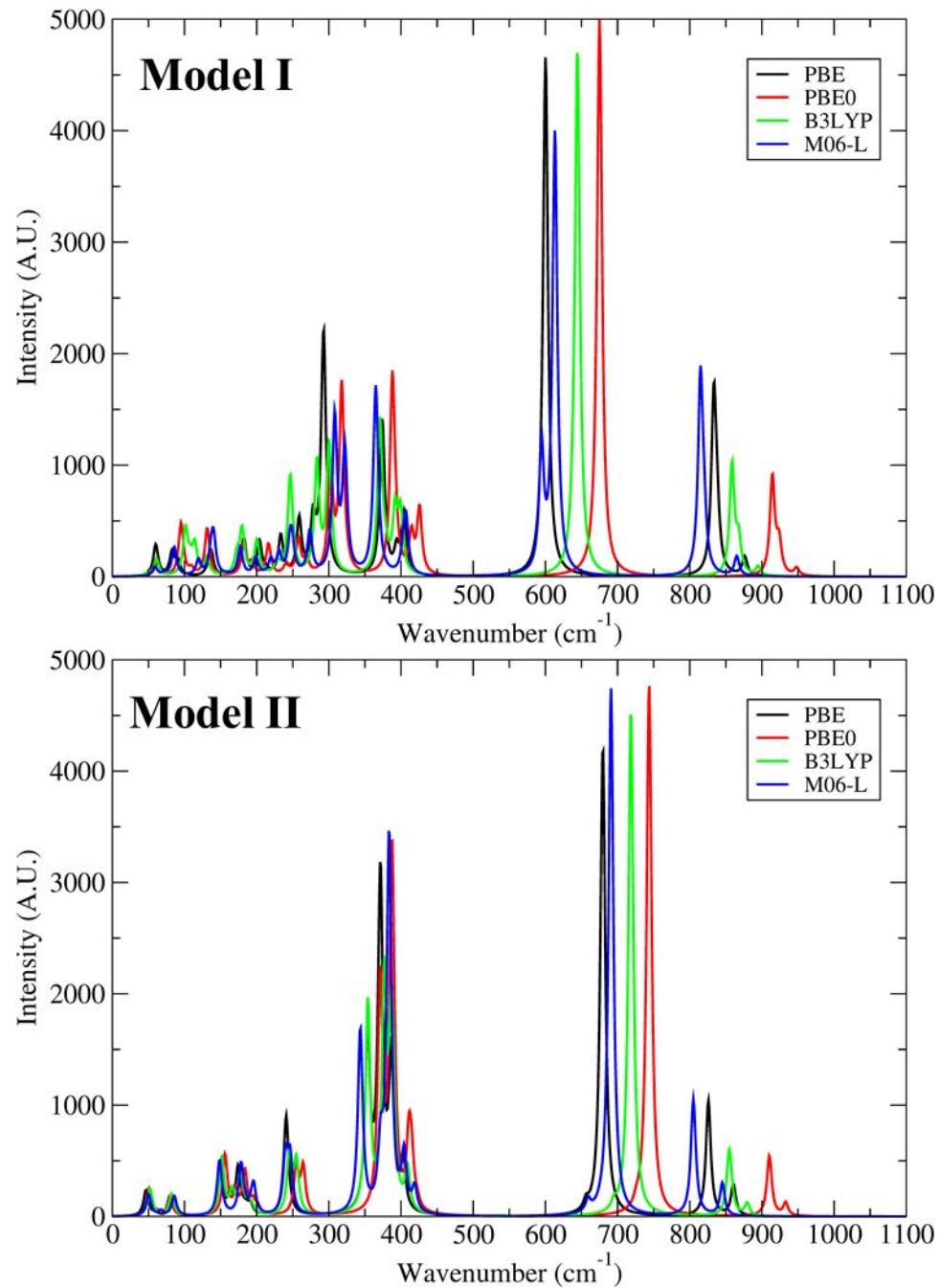
**Figure S8.** Computed IR spectra of Model I – VI of  $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$  using different levels of theory in aqueous solution.

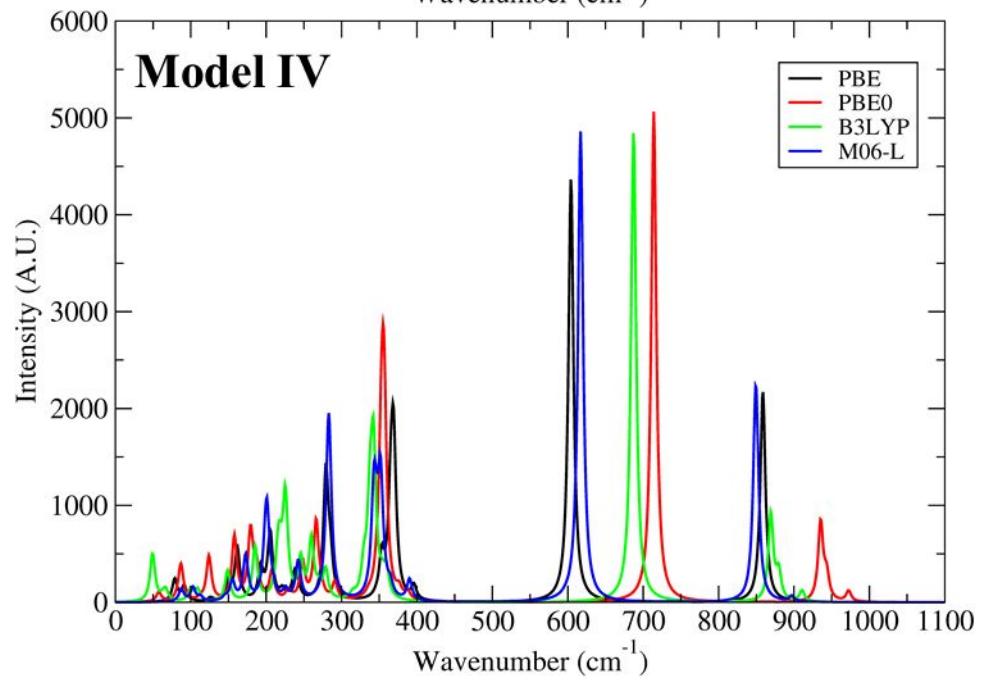
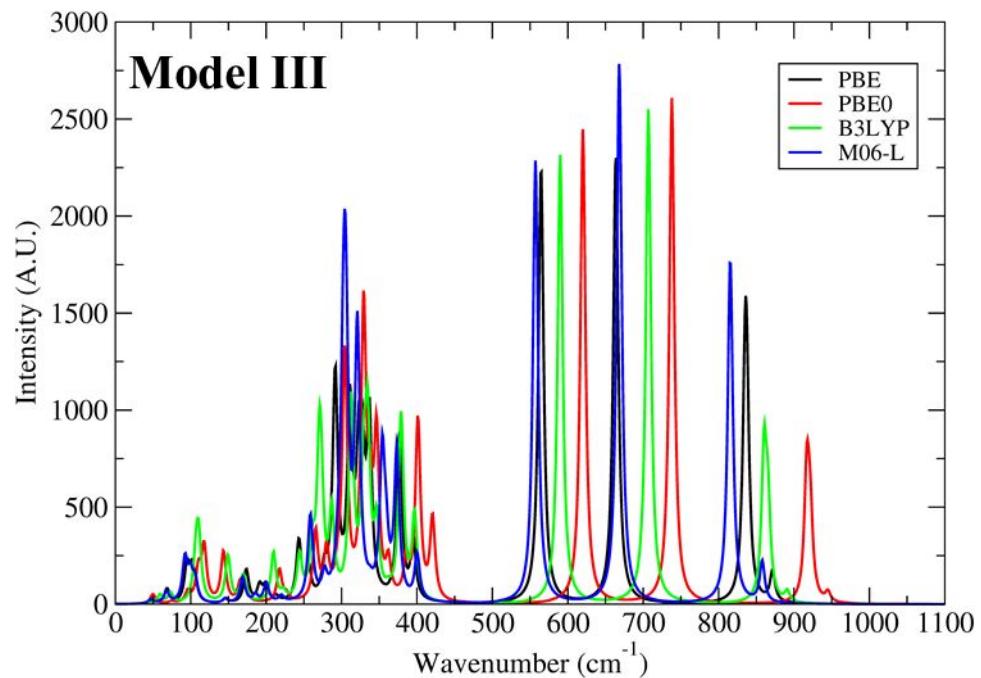


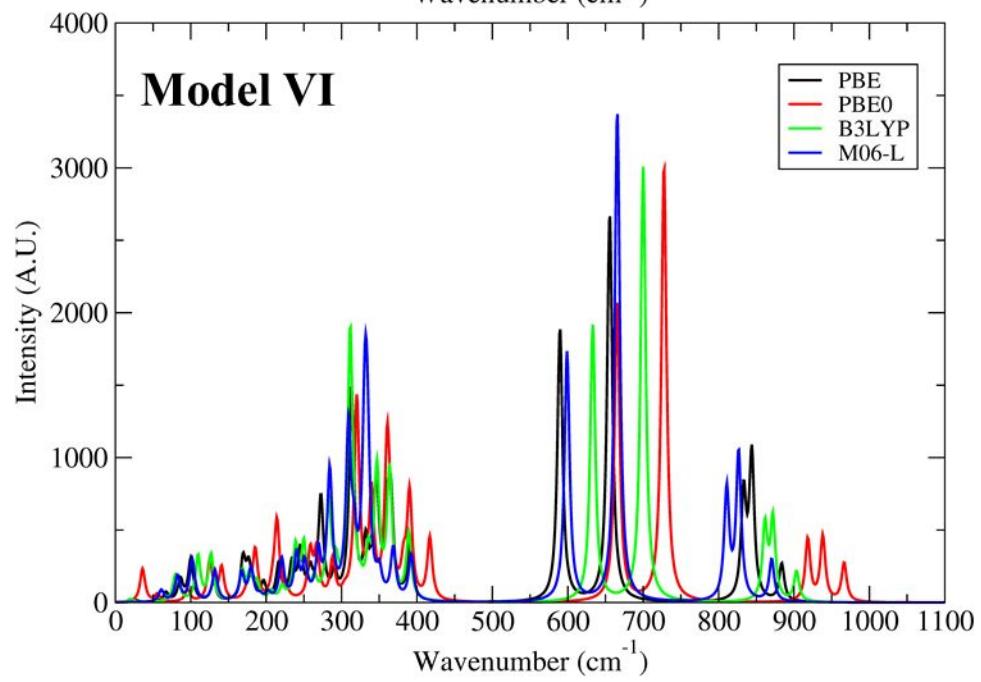
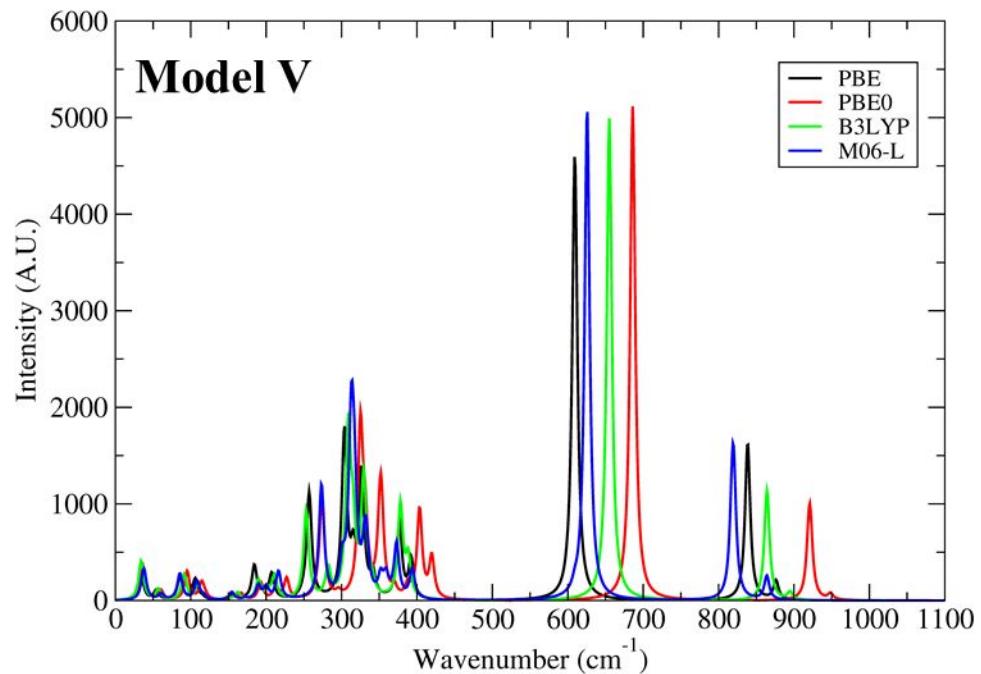




**Figure S9.** Computed IR spectra of Model I – VI of  $\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$  using different levels of theory in aqueous solution.







**Table S9.** Total Electronic Energies (in Hartree) of six different models of  $\text{Ca}_2[\text{M(VI)}\text{O}_2(\text{O}_2)_3]$  ( $\text{M} = \text{Np, U}$ ) and  $\text{Ca}_2[\text{Np(V)}\text{O}_2(\text{O}_2)_3]^-$  at different levels of theory in aqueous solution.

<b>Model</b>	<b>Functional</b>	$\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$	$\text{Ca}_2[\text{U(VI)}\text{O}_2(\text{O}_2)_3]$	$\text{Ca}_2[\text{Np(V)}\text{O}_2(\text{O}_2)_3]^-$
Model I	PBE	-2471.1533465	-2433.6830277	-2471.2413798
	PBE0	-2471.0700005	-2433.6268199	-2471.1862758
	M06-L	-2472.1064363	-2434.6163216	-2472.2003441
Model II	B3LYP	-2472.1925185	-2434.7395684	-2472.3156828
	PBE	-2471.135611	-2433.6655647	-2471.2540092
	PBE0	-2471.0510984	-2433.6160465	-2471.1927133
Model III	M06-L	-2472.0916359	-2434.6021725	-2472.2208904
	B3LYP	-2472.1731845	-2434.7288455	-2472.3203768
	PBE	-2471.1578304	-2433.686578	-2471.2515564
Model IV	PBE0	-2471.0744667	-2433.6319195	-
	M06-L	-2472.1107876	-2434.6198192	-2472.2186648
	B3LYP	-2472.1862002	-2434.7437593	-2472.3214331
Model V	PBE	-2471.1465319	-2433.672637	-2471.2347688
	PBE0	-2471.0625113	-2433.6129282	-2471.1748598
	M06-L	-2472.1008538	-2434.6055292	-2472.1989484
Model VI	B3LYP	-2472.1842317	-2434.7254689	-2472.2969271
	PBE	-2471.1593937	-2433.6889091	-2471.2500209
	PBE0	-2471.0738133	-2433.6339449	-2471.1927132
Model VI	M06-L	-2472.1118226	-2434.6219009	-2472.2083125
	B3LYP	-2472.1876339	-2434.7455836	-2472.3203767
	PBE	-2471.1534256	-2433.6769221	-2471.2440396
Model VI	PBE0	-2471.0685737	-2433.6236737	-2471.1859974
	M06-L	-2472.107439	-2434.6104676	-2472.2112352
	B3LYP	-2472.190467	-2434.735863	-2472.3134942

### III. Crystallographic Details

**Table S10.** Crystal parameters, data collection and structure refinement details.

<b>Crystal data</b>	
Chemical formula	<chem>Ca2NpO17</chem>
M <sub>r</sub>	589.16
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	120
a, b, c (Å)	9.5263 (17), 12.022 (2), 12.224 (2)
V (Å <sup>3</sup> )	1400.0 (4)
Z	4
Radiation type	Mo Kα
μ (mm <sup>-1</sup> )	8.24
Crystal size (mm)	0.1 × 0.02 × 0.02
<b>Data collection</b>	
Diffractometer	Bruker APEX-II CCD
Absorption correction	Multi-scan
T <sub>min</sub> , T <sub>max</sub>	0.622, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	4047, 1688, 1112
R <sub>int</sub>	0.053
<b>Refinement</b>	
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.049, 0.105, 1.09
No. of reflections	1688
No. of parameters	96
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	2.37, -1.22

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick 2008), *SHELXL2014/7* (Sheldrick, 2014).

**Table S11.** Fractional atomic coordinates, isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ ), and site occupancy (if less than 1).

	x	y	z	$U_{\text{iso}}^*$ / $U_{\text{eq}}$	Occ. (<1)
Np1	0.5	0.64674 (4)	0.25	0.00830 (16)	
O1	0.3134 (8)	0.6429 (6)	0.2897 (6)	0.0121 (15)	
O2	0.5238 (8)	0.5036 (7)	0.3722 (7)	0.023 (2)	
O3	0.4495 (8)	0.6127 (8)	0.0703 (6)	0.025 (2)	
O4	0.4823 (11)	0.8257 (7)	0.1904 (7)	0.037 (3)	
O5	0.8432 (8)	0.5106 (7)	0.3643 (7)	0.024 (2)	
O6	0.6926 (9)	0.2788 (6)	0.4224 (7)	0.0244 (19)	
O7	0.9171 (10)	0.3826 (9)	0.5628 (9)	0.048 (3)	
O8	0.7688 (11)	0.6203 (7)	0.6114 (10)	0.047 (3)	
O9	0.5381 (16)	0.3057 (14)	0.2142 (15)	0.029 (5)	0.5
Ca1	0.6839 (2)	0.4587 (2)	0.5179 (2)	0.0210 (5)	

**Table S12.** Atomic displacement parameters ( $\text{\AA}^2$ ).

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Np1	0.0069 (3)	0.0079 (3)	0.0101 (3)	0	0.0001 (3)	0
O1	0.010 (4)	0.016 (4)	0.011 (3)	-0.004 (3)	0.004 (3)	0.001 (3)
O2	0.014 (5)	0.027 (4)	0.029 (4)	0.008 (4)	0.008 (4)	0.018 (4)
O3	0.014 (4)	0.049 (6)	0.012 (4)	-0.002 (4)	-0.001 (3)	-0.006 (4)
O4	0.033 (6)	0.025 (4)	0.052 (6)	0.018 (5)	0.026 (5)	0.018 (4)
O5	0.017 (5)	0.024 (5)	0.030 (5)	-0.002 (4)	0.002 (4)	0.008 (4)
O6	0.024 (5)	0.018 (4)	0.032 (5)	0.006 (4)	0.000 (4)	0.005 (4)
O7	0.019 (5)	0.073 (8)	0.051 (7)	0.006 (5)	-0.001 (5)	0.046 (6)
O8	0.040 (6)	0.026 (5)	0.077 (8)	-0.012 (5)	-0.036 (6)	0.015 (5)
O9	0.014 (11)	0.030 (9)	0.042 (12)	0.006 (7)	-0.008 (7)	0.003 (8)
Ca1	0.0091 (11)	0.0308 (13)	0.0231 (12)	0.0006 (11)	0.0001 (10)	0.0138 (10)

**Table S13.** Bond distances and angles (Å, °)

Np1—O1 <sup>i</sup>	1.843 (7)	O3—Ca1 <sup>ii</sup>	2.476 (8)
Np1—O1	1.843 (7)	O3—Ca1 <sup>i</sup>	2.491 (9)
Np1—O4	2.278 (8)	O4—O4 <sup>i</sup>	1.496 (19)
Np1—O4 <sup>i</sup>	2.278 (8)	O5—Ca1	2.494 (8)
Np1—O3	2.286 (8)	O6—Ca1	2.460 (8)
Np1—O3 <sup>i</sup>	2.286 (8)	O7—Ca1	2.465 (9)
Np1—O2 <sup>i</sup>	2.290 (7)	O8—Ca1	2.393 (10)
Np1—O2	2.290 (7)	O9—O9 <sup>i</sup>	1.14 (3)
Np1—Ca1 <sup>ii</sup>	3.567 (2)	Ca1—O2 <sup>iii</sup>	2.434 (8)
Np1—Ca1 <sup>iii</sup>	3.567 (2)	Ca1—O3 <sup>iv</sup>	2.476 (8)
O1—Ca1 <sup>iii</sup>	2.650 (7)	Ca1—O3 <sup>i</sup>	2.491 (9)
O2—O3 <sup>i</sup>	1.510 (12)	Ca1—O1 <sup>iii</sup>	2.649 (7)
O2—Ca1	2.406 (8)	Ca1—Np1 <sup>iii</sup>	3.567 (2)
O2—Ca1 <sup>iii</sup>	2.434 (8)	Ca1—Ca1 <sup>iii</sup>	3.668 (5)
O3—O2 <sup>i</sup>	1.510 (12)		
O1 <sup>i</sup> —Np1—O1	177.1 (4)	Ca1 <sup>ii</sup> —O3—Ca1 <sup>i</sup>	95.2 (3)
O1 <sup>i</sup> —Np1—O4	90.6 (3)	O4 <sup>i</sup> —O4—Np1	70.8 (2)
O1—Np1—O4	92.1 (3)	O8—Ca1—O2	112.7 (3)
O1 <sup>i</sup> —Np1—O4 <sup>i</sup>	92.1 (3)	O8—Ca1—O2 <sup>iii</sup>	82.0 (4)
O1—Np1—O4 <sup>i</sup>	90.6 (3)	O2—Ca1—O2 <sup>iii</sup>	81.5 (3)
O4—Np1—O4 <sup>i</sup>	38.3 (5)	O8—Ca1—O6	158.2 (3)
O1 <sup>i</sup> —Np1—O3	86.8 (3)	O2—Ca1—O6	82.3 (3)
O1—Np1—O3	92.6 (3)	O2 <sup>iii</sup> —Ca1—O6	116.9 (3)
O4—Np1—O3	81.1 (3)	O8—Ca1—O7	83.7 (4)
O4 <sup>i</sup> —Np1—O3	119.5 (3)	O2—Ca1—O7	145.0 (3)
O1 <sup>i</sup> —Np1—O3 <sup>i</sup>	92.6 (3)	O2 <sup>iii</sup> —Ca1—O7	132.8 (3)
O1—Np1—O3 <sup>i</sup>	86.8 (3)	O6—Ca1—O7	75.5 (4)
O4—Np1—O3 <sup>i</sup>	119.5 (3)	O8—Ca1—O3 <sup>iv</sup>	117.6 (4)
O4 <sup>i</sup> —Np1—O3 <sup>i</sup>	81.1 (3)	O2—Ca1—O3 <sup>iv</sup>	72.4 (3)
O3—Np1—O3 <sup>i</sup>	159.4 (5)	O2 <sup>iii</sup> —Ca1—O3 <sup>iv</sup>	35.8 (3)
O1 <sup>i</sup> —Np1—O2 <sup>i</sup>	84.5 (3)	O6—Ca1—O3 <sup>iv</sup>	81.3 (3)
O1—Np1—O2 <sup>i</sup>	93.3 (3)	O7—Ca1—O3 <sup>iv</sup>	128.8 (3)

O4—Np1—O2 <sup>i</sup>	119.6 (3)	O8—Ca1—O3 <sup>i</sup>	77.1 (3)
O4 <sup>i</sup> —Np1—O2 <sup>i</sup>	157.8 (3)	O2—Ca1—O3 <sup>i</sup>	35.9 (3)
O3—Np1—O2 <sup>i</sup>	38.5 (3)	O2 <sup>iii</sup> —Ca1—O3 <sup>i</sup>	71.7 (3)
O3 <sup>i</sup> —Np1—O2 <sup>i</sup>	120.9 (3)	O6—Ca1—O3 <sup>i</sup>	117.7 (3)
O1 <sup>i</sup> —Np1—O2	93.3 (3)	O7—Ca1—O3 <sup>i</sup>	146.3 (3)
O1—Np1—O2	84.5 (3)	O3 <sup>iv</sup> —Ca1—O3 <sup>i</sup>	84.8 (3)
O4—Np1—O2	157.8 (3)	O8—Ca1—O5	87.2 (4)
O4 <sup>i</sup> —Np1—O2	119.6 (3)	O2—Ca1—O5	76.8 (3)
O3—Np1—O2	120.9 (3)	O2 <sup>iii</sup> —Ca1—O5	149.7 (3)
O3 <sup>i</sup> —Np1—O2	38.5 (3)	O6—Ca1—O5	80.9 (3)
O2 <sup>i</sup> —Np1—O2	82.6 (4)	O7—Ca1—O5	73.3 (3)
O1 <sup>i</sup> —Np1—Ca1 <sup>ii</sup>	46.2 (2)	O3 <sup>iv</sup> —Ca1—O5	146.1 (3)
O1—Np1—Ca1 <sup>ii</sup>	132.4 (2)	O3 <sup>i</sup> —Ca1—O5	78.4 (3)
O4—Np1—Ca1 <sup>ii</sup>	96.8 (2)	O8—Ca1—O1 <sup>iii</sup>	87.0 (3)
O4 <sup>i</sup> —Np1—Ca1 <sup>ii</sup>	123.6 (2)	O2—Ca1—O1 <sup>iii</sup>	140.0 (3)
O3—Np1—Ca1 <sup>ii</sup>	43.6 (2)	O2 <sup>iii</sup> —Ca1—O1 <sup>iii</sup>	66.7 (2)
O3 <sup>i</sup> —Np1—Ca1 <sup>ii</sup>	126.7 (2)	O6—Ca1—O1 <sup>iii</sup>	90.9 (3)
O2 <sup>i</sup> —Np1—Ca1 <sup>ii</sup>	42.5 (2)	O7—Ca1—O1 <sup>iii</sup>	67.8 (3)
O2—Np1—Ca1 <sup>ii</sup>	101.7 (2)	O3 <sup>iv</sup> —Ca1—O1 <sup>iii</sup>	67.6 (3)
O1 <sup>i</sup> —Np1—Ca1 <sup>iii</sup>	132.4 (2)	O3 <sup>i</sup> —Ca1—O1 <sup>iii</sup>	137.0 (3)
O1—Np1—Ca1 <sup>iii</sup>	46.2 (2)	O5—Ca1—O1 <sup>iii</sup>	141.1 (3)
O4—Np1—Ca1 <sup>iii</sup>	123.6 (2)	O8—Ca1—Np1 <sup>iii</sup>	94.3 (3)
O4 <sup>i</sup> —Np1—Ca1 <sup>iii</sup>	96.8 (2)	O2—Ca1—Np1 <sup>iii</sup>	110.9 (2)
O3—Np1—Ca1 <sup>iii</sup>	126.7 (2)	O2 <sup>iii</sup> —Ca1—Np1 <sup>iii</sup>	39.48 (18)
O3 <sup>i</sup> —Np1—Ca1 <sup>iii</sup>	43.6 (2)	O6—Ca1—Np1 <sup>iii</sup>	94.7 (2)
O2 <sup>i</sup> —Np1—Ca1 <sup>iii</sup>	101.7 (2)	O7—Ca1—Np1 <sup>iii</sup>	97.7 (2)
O2—Np1—Ca1 <sup>iii</sup>	42.5 (2)	O3 <sup>iv</sup> —Ca1—Np1 <sup>iii</sup>	39.51 (19)
Ca1 <sup>ii</sup> —Np1—Ca1 <sup>iii</sup>	138.35 (9)	O3 <sup>i</sup> —Ca1—Np1 <sup>iii</sup>	111.0 (2)
Np1—O1—Ca1 <sup>iii</sup>	103.7 (3)	O5—Ca1—Np1 <sup>iii</sup>	170.6 (2)
O3 <sup>i</sup> —O2—Np1	70.6 (4)	O1 <sup>iii</sup> —Ca1—Np1 <sup>iii</sup>	30.14 (16)
O3 <sup>i</sup> —O2—Ca1	75.1 (5)	O8—Ca1—Ca1 <sup>iii</sup>	99.2 (3)
Np1—O2—Ca1	135.6 (4)	O2—Ca1—Ca1 <sup>iii</sup>	41.00 (19)
O3 <sup>i</sup> —O2—Ca1 <sup>iii</sup>	73.6 (4)	O2 <sup>iii</sup> —Ca1—Ca1 <sup>iii</sup>	40.4 (2)
Np1—O2—Ca1 <sup>iii</sup>	98.0 (3)	O6—Ca1—Ca1 <sup>iii</sup>	102.3 (2)

Ca1—O2—Ca1 <sup>iii</sup>	98.5 (3)	O7—Ca1—Ca1 <sup>iii</sup>	171.2 (2)
O2 <sup>i</sup> —O3—Np1	70.9 (4)	O3 <sup>iv</sup> —Ca1—Ca1 <sup>iii</sup>	42.6 (2)
O2 <sup>i</sup> —O3—Ca1 <sup>ii</sup>	70.6 (4)	O3 <sup>i</sup> —Ca1—Ca1 <sup>iii</sup>	42.25 (19)
Np1—O3—Ca1 <sup>ii</sup>	96.9 (3)	O5—Ca1—Ca1 <sup>iii</sup>	115.0 (2)
O2 <sup>i</sup> —O3—Ca1 <sup>i</sup>	69.0 (4)	O1 <sup>iii</sup> —Ca1—Ca1 <sup>iii</sup>	103.89 (19)
Np1—O3—Ca1 <sup>i</sup>	131.0 (4)	Np1 <sup>iii</sup> —Ca1—Ca1 <sup>iii</sup>	73.86 (7)
O4—Np1—O1—Ca1 <sup>iii</sup>	-137.1 (3)	O2 <sup>i</sup> —Np1—O1—Ca1 <sup>iii</sup>	103.1 (3)
O4 <sup>i</sup> —Np1—O1—Ca1 <sup>iii</sup>	-98.8 (3)	O2—Np1—O1—Ca1 <sup>iii</sup>	20.9 (3)
O3—Np1—O1—Ca1 <sup>iii</sup>	141.7 (3)	Ca1 <sup>ii</sup> —Np1—O1— Ca1 <sup>iii</sup>	121.8 (2)
O3 <sup>i</sup> —Np1—O1—Ca1 <sup>iii</sup>	-17.7 (3)		

Symmetry codes: (i)  $-x+1, y, -z+1/2$ ; (ii)  $x, -y+1, z-1/2$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $x, -y+1, z+1/2$ .

#### IV. XYZ coordinates for the DFT-optimized $\text{Ca}_2[\text{Np(VI)}\text{O}_2(\text{O}_2)_3]$ models

##### Model I

PBE	x	y	z
Np	0.54165700	0.00000000	0.00000700
O	0.40889700	1.91591900	0.00003700
O	0.40889700	-1.91591900	-0.00002400
O	-1.82809200	-0.00008800	0.74923400
O	2.30140700	-0.00000900	1.47701000
O	-1.82808800	0.00008800	-0.74927400
O	1.04251500	-0.00000400	-2.20100500
O	2.30139600	0.00000900	-1.47701000
O	1.04253000	0.00000400	2.20101500
Ca	-2.02924400	-2.24370400	-0.00020100
Ca	-2.02924500	2.24370400	0.00017700

##### PBE0

Np	0.54054300	-0.00000300	0.00000100
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O	0.47405800	1.83912500	-0.14477200
O	0.47406700	-1.83913500	0.14476300
O	-1.81358500	0.03181800	0.73433200
O	2.28504100	0.09516200	1.44628700
O	-1.81358200	-0.03182800	-0.73434400
O	1.04805100	-0.14228900	-2.17200500
O	2.28503600	-0.09512100	-1.44628500
O	1.04805000	0.14232000	2.17199800
Ca	-2.05417600	-2.23784400	0.03643300
Ca	-2.05420100	2.23783700	-0.03642700

#### M06-L

Np	0.54364000	0.00000000	0.00000000
O	0.42214700	1.88635800	0.00000000
O	0.42214700	-1.88635800	0.00000000
O	-1.83731800	0.00000000	0.74844000
O	2.31847200	0.00000000	1.49016800
O	-1.83732300	0.00000000	-0.74843200
O	1.06494700	0.00000000	-2.21023400
O	2.31847200	0.00000000	-1.49016700
O	1.06494600	0.00000000	2.21023300
Ca	-2.05126200	-2.23341600	-0.00000100
Ca	-2.05126200	2.23341600	-0.00000100

#### B3LYP

Np	0.55279000	-0.00000100	0.00000100
O	0.45697700	1.87442200	0.00006600
O	0.45697700	-1.87441800	-0.00008700
O	-1.84255700	-0.00001600	0.74763000
O	2.30262800	-0.00007900	1.49680000
O	-1.84255700	0.00005600	-0.74763300

O	1.03351900	0.00007100	-2.21281500
O	2.30264700	0.00005700	-1.49678800
O	1.03350700	-0.00011200	2.21282700
Ca	-2.06548800	-2.24310900	-0.00003500
Ca	-2.06544300	2.24312400	0.00003200

### Model II

#### PBE

Np	0.00000700	0.41779800	0.00000000
O	-0.00004200	0.38745300	-1.86895100
O	0.00000900	0.38750000	1.86895100
O	-2.37875700	0.02736800	0.00001100
O	0.72343100	2.59359300	-0.00002700
O	-1.64545900	-1.27868000	0.00001500
O	1.64546600	-1.27865600	-0.00000400
O	2.37876200	0.02739300	-0.00001700
O	-0.72349500	2.59356000	0.00000600
Ca	3.91385000	-1.66328300	0.00000400
Ca	-3.91384700	-1.66328800	0.00000100

#### PBE0

Np	-0.00000200	0.44083900	0.00000100
O	0.00000800	0.42200600	-1.81732700
O	-0.00001200	0.42198000	1.81732900
O	-2.30980900	-0.01597700	-0.00000600
O	0.72140000	2.59174600	0.00000400
O	-1.58934300	-1.29289600	-0.00001400
O	1.58931900	-1.29292400	0.00001300
O	2.30979100	-0.01600900	0.00001600
O	-0.72130000	2.59179100	-0.00000400
Ca	3.84255400	-1.70690500	-0.00000800

Ca -3.84256800 -1.70688500 -0.00000100

**M06-L**

Np 0.00000000 0.40301400 -0.00000200  
O -0.00011800 0.37946500 -1.84129500  
O 0.00009300 0.37949900 1.84129000  
O -2.40597400 0.04749500 0.00006000  
O 0.72065300 2.59975700 -0.00005200  
O -1.68989700 -1.26213900 0.00003300  
O 1.68991200 -1.26209800 -0.00002100  
O 2.40598700 0.04753600 -0.00005400  
O -0.72064600 2.59976300 0.00005000  
Ca 3.95686800 -1.64287100 0.00000600  
Ca -3.95687200 -1.64285300 0.00000100

**B3LYP**

Np -0.00000300 0.44608900 -0.00000100  
O -0.00003700 0.41175300 -1.84421700  
O 0.00004100 0.41176500 1.84421400  
O -2.34315000 -0.01275800 0.00000400  
O 0.73257700 2.62537100 -0.00002800  
O -1.60739700 -1.31052500 0.00000700  
O 1.60737700 -1.31055900 -0.00000200  
O 2.34313400 -0.01279500 -0.00002100  
O -0.73247700 2.62541800 0.00003800  
Ca 3.87572700 -1.72270000 0.00000300  
Ca -3.87573800 -1.72268400 0.00000500

**Model III**

**PBE**

Np -0.00002900 -0.52531500 -0.11536100  
O 0.00009700 -2.13487900 -1.07640700

O	0.00008500	1.22197800	0.78187000
O	-0.72023000	-1.57023400	1.75742900
O	-1.78945800	0.37677800	-1.37082000
O	0.71986000	-1.57033500	1.75754500
O	2.38886900	-0.28634400	-0.19134700
O	1.78955000	0.37667000	-1.37075100
O	-2.38889600	-0.28615300	-0.19143900
Ca	-2.25073500	1.99594000	0.24897900
Ca	2.25092000	1.99578000	0.24901900

#### PBE0

Np	0.03983700	-0.55600400	-0.10161900
O	0.15506900	-2.00443100	-1.17957800
O	-0.07760600	1.01550800	0.92255200
O	-0.49854800	-1.82795100	1.66950400
O	-1.65509800	0.43818200	-1.35615800
O	0.92266600	-1.67612600	1.62684400
O	2.29342700	0.01658300	-0.41333800
O	1.48699900	0.70944600	-1.40560100
O	-2.30917000	-0.34426100	-0.31722200
Ca	-2.32429200	1.87025900	0.33156000
Ca	2.01195400	2.18437900	0.32216700

#### M06-L

Np	-0.00000400	0.52395400	-0.12387100
O	-0.00001000	2.12998200	-1.04678500
O	-0.00000200	-1.21184600	0.72715100
O	0.71678800	1.53381300	1.78745300
O	1.84453700	-0.34492800	-1.35921100
O	-0.71682200	1.53380900	1.78744900
O	-2.41287200	0.29833400	-0.16387900

O	-1.84452400	-0.34493300	-1.35923000
O	2.41287100	0.29836300	-0.16386800
Ca	2.27121600	-1.99669400	0.24618200
Ca	-2.27118200	-1.99672800	0.24618600

### B3LYP

Np	-0.04989300	0.56181900	-0.09495200
O	-0.19231900	2.00676900	-1.23722900
O	0.11397400	-1.02317600	0.97440900
O	0.53028900	1.87897600	1.65848200
O	1.67069500	-0.47044600	-1.40936700
O	-0.91653500	1.72021000	1.64711800
O	-2.32437900	-0.03667000	-0.41248100
O	-1.52105900	-0.74037900	-1.43794200
O	2.30489800	0.37005000	-0.36646600
Ca	2.36197500	-1.86351000	0.33478200
Ca	-1.99619900	-2.23108200	0.34013400

### Model IV

#### PBE

Np	0.00000300	0.46614100	0.00000400
O	0.95825500	0.42770400	-1.64188300
O	-0.95829800	0.42771300	1.64186600
O	2.11519700	0.36239100	1.11715800
O	-0.60287700	-1.81585700	-0.40784800
O	1.70879400	1.73208800	0.85284900
O	-1.70878400	1.73208300	-0.85287000
O	-2.11518400	0.36238400	-1.11717200
O	0.60287800	-1.81584900	0.40786900
Ca	2.81784800	-1.36631400	-0.35387600
Ca	-2.81785300	-1.36630700	0.35386700

**PBE0**

Np	-0.00000300	0.45338200	0.00000000
O	0.88183400	0.42363200	-1.60241100
O	-0.88181200	0.42361400	1.60242400
O	2.10299700	0.41458600	1.05787700
O	-0.60090000	-1.78884200	-0.38884400
O	1.68398100	1.76239900	0.79129900
O	-1.68399200	1.76239300	-0.79129700
O	-2.10300100	0.41457900	-1.05788200
O	0.60090700	-1.78884800	0.38883300
Ca	2.82736000	-1.37881300	-0.33640800
Ca	-2.82735100	-1.37881800	0.33640800

**M06-L**

Np	0.00000300	0.48041600	0.00000200
O	0.95383100	0.43879900	-1.61256000
O	-0.95387300	0.43881300	1.61253800
O	2.11605600	0.32745900	1.12272100
O	-0.60288700	-1.81688500	-0.40159100
O	1.75609600	1.70872200	0.89393300
O	-1.75608600	1.70871900	-0.89393900
O	-2.11604400	0.32745700	-1.12272800
O	0.60288400	-1.81687800	0.40160500
Ca	2.81648300	-1.38021300	-0.37629300
Ca	-2.81649000	-1.38020500	0.37629300

**B3LYP**

Np	-0.00000200	-0.45083500	-0.00000900
O	-0.89405500	-0.41473100	-1.63086000
O	0.89402500	-0.41466000	1.63086000

O	-2.14180700	-0.43192900	1.06821600
O	0.61384600	1.82859200	-0.39133100
O	-1.69692300	-1.79369500	0.78322000
O	1.69695900	-1.79369200	-0.78314900
O	2.14186500	-0.43193000	-1.06816400
O	-0.61385300	1.82860700	0.39131400
Ca	-2.84598000	1.37287400	-0.33718600
Ca	2.84596600	1.37288400	0.33718800

#### Model V

##### PBE

Np	0.00000600	0.22677900	0.00000700
O	-1.29516900	0.14026400	-1.40541000
O	1.29516800	0.14033600	1.40544300
O	-1.87735300	-0.10791100	1.43860000
O	0.53656500	2.37883400	-0.48138900
O	-1.32470400	-1.41978900	1.02159000
O	1.32473400	-1.41974800	-1.02166000
O	1.87736600	-0.10784100	-1.43861000
O	-0.53667000	2.37883100	0.48135300
Ca	3.17605600	-0.92385800	0.31387200
Ca	-3.17606000	-0.92385700	-0.31387300

##### PBE0

Np	0.00000000	0.27855500	0.00000300
O	-1.28998300	0.22753900	-1.31713600
O	1.28998200	0.22749100	1.31714500
O	-1.75522800	-0.22248200	1.41543500
O	0.50632700	2.42914700	-0.51711000
O	-1.20944000	-1.47902800	0.94512700
O	1.20941600	-1.47903000	-0.94514700

O	1.75522200	-0.22248800	-1.41543900
O	-0.50624800	2.42914800	0.51711200
Ca	3.12995600	-1.02971200	0.27989700
Ca	-3.12997600	-1.02968600	-0.27990600

#### M06-L

Np	0.00000600	0.22226900	0.00000600
O	-1.27380800	0.14027100	-1.38835300
O	1.27384800	0.14043400	1.38834300
O	-1.89950300	-0.11218100	1.43624100
O	0.53608300	2.39354100	-0.47751800
O	-1.35097500	-1.41704600	1.01397000
O	1.35106800	-1.41695600	-1.01401700
O	1.89954700	-0.11204800	-1.43622600
O	-0.53642100	2.39347700	0.47750000
Ca	3.19596500	-0.91864800	0.32361200
Ca	-3.19592700	-0.91869800	-0.32361700

#### B3LYP

Np	0.00000100	0.29152800	0.00000400
O	-1.27695500	0.20757100	-1.38716800
O	1.27696700	0.20751200	1.38717000
O	-1.82560300	-0.16815700	1.43707100
O	0.53527100	2.44226800	-0.49444800
O	-1.23952100	-1.46250300	1.01435400
O	1.23948500	-1.46253200	-1.01436200
O	1.82557200	-0.16818900	-1.43707100
O	-0.53516400	2.44229800	0.49443100
Ca	3.13747400	-1.08547000	0.30266700
Ca	-3.13750000	-1.08544400	-0.30267600

#### Model VI

**PBE**

Np	-0.01102600	-0.51750300	-0.02538700
O	-0.15337500	1.37867100	-0.48587400
O	0.10613500	-2.32967900	0.45356900
O	-2.26184200	-0.31227800	0.82161100
O	1.51862500	0.17466300	1.58015200
O	-2.28613200	-0.61699300	-0.62402900
O	1.21354300	-0.81176800	-1.93453500
O	2.18818300	-0.43757000	-0.92346300
O	0.19285600	0.22117100	2.16047700
Ca	-2.56786100	1.70236600	-0.29507400
Ca	2.41193300	1.79753400	-0.00604000

**PBE0**

Np	-0.01700700	-0.50681800	-0.00418700
O	-0.11315800	1.31482600	-0.44208400
O	0.06521800	-2.26881400	0.43257600
O	-2.24137300	-0.28775000	0.81394600
O	1.57727300	0.12824400	1.52180600
O	-2.27998100	-0.56630700	-0.61516700
O	1.02772000	-0.79419500	-2.00482500
O	2.04431000	-0.47496500	-1.04577200
O	0.29263200	0.20376300	2.14112000
Ca	-2.55955700	1.72042800	-0.26845100
Ca	2.48958300	1.73435400	-0.03272100

**M06-L**

Np	-0.01198200	-0.52569200	-0.02459000
O	-0.14521000	1.33827900	-0.49614300
O	0.10517200	-2.30461400	0.48371700

O -2.27887500 -0.30700300 0.81462200  
 O 1.50738700 0.22321500 1.59123400  
 O -2.29682200 -0.62070800 -0.62161500  
 O 1.27755100 -0.83540800 -1.91235300  
 O 2.22184800 -0.44170900 -0.88925900  
 O 0.18591300 0.27727100 2.16579800  
 Ca -2.57583200 1.70271200 -0.31837000  
 Ca 2.40076400 1.81002800 -0.02168600

### B3LYP

Np -0.01464100 -0.50787000 -0.00598600  
 O -0.12656000 1.33669300 -0.49964700  
 O 0.08847500 -2.28586200 0.47989900  
 O -2.28123500 -0.31412600 0.80873300  
 O 1.57197600 0.18197200 1.55962600  
 O -2.30352300 -0.61422800 -0.64066400  
 O 1.11539800 -0.85656900 -1.97832900  
 O 2.12621800 -0.49681700 -0.99234200  
 O 0.25514800 0.25494100 2.16404100  
 Ca -2.60380900 1.71654600 -0.28635200  
 Ca 2.49353200 1.76264700 -0.04634200

## Ca<sub>2</sub>[U(VI)O<sub>2</sub>(O<sub>2</sub>)<sub>3</sub>] Geometries

### Model I

#### PBE

U 0.55031200 0.00001900 0.00000000  
 O 0.35966600 1.93754200 -0.00003000  
 O 0.35989500 -1.93751800 0.00004000  
 O -1.74904900 -0.00008200 0.74755600  
 O 2.23208000 0.00011900 1.49302700

O -1.74902000 -0.00009200 -0.74762000  
O 0.96204100 -0.00001500 -2.22440500  
O 2.23209300 0.00008100 -1.49301200  
O 0.96202300 0.00007900 2.22441000  
Ca -1.98756200 -2.30051600 0.00001900  
Ca -1.98776500 2.30038100 -0.00000500

#### PBE0

U 0.55349500 -0.01916800 -0.00000200  
O 0.44631100 1.86735500 0.00000100  
O 0.31050300 -1.88599600 0.00000900  
O -1.71516300 0.04784800 0.73188300  
O 2.22903300 -0.07641900 1.47191000  
O -1.71519300 0.04785500 -0.73182300  
O 0.98097600 -0.03195700 -2.19773800  
O 2.22902200 -0.07642500 -1.47191900  
O 0.98099000 -0.03193900 2.19773600  
Ca -2.12627300 -2.17921700 -0.00000400  
Ca -1.91839400 2.32325900 -0.00000900

#### M06-L

U 0.56509000 -0.02302100 0.00000100  
O 0.44092000 1.89412000 0.00002300  
O 0.26418700 -1.91812800 -0.00002400  
O -1.74538700 0.05911200 0.74471000  
O 2.25129700 -0.08273800 1.51286900  
O -1.74539200 0.05913200 -0.74466300  
O 0.98620700 -0.03196900 -2.23719600  
O 2.25120600 -0.08268300 -1.51296900  
O 0.98633900 -0.03202700 2.23717700  
Ca -2.15113300 -2.17094200 0.00000200

Ca -1.92403100 2.33091200 0.00002300

**B3LYP**

U 0.56199000 -0.02380100 0.00000200  
O 0.46602100 1.88826700 0.00001200  
O 0.28567200 -1.91180700 -0.00001000  
O -1.74508000 0.06731300 0.74425200  
O 2.25815700 -0.09920800 1.48571800  
O -1.74509000 0.06734700 -0.74416900  
O 0.99061100 -0.04061600 -2.22392900  
O 2.25803700 -0.09913200 -1.48585700  
O 0.99079100 -0.04065200 2.22390400  
Ca -2.17562700 -2.17848800 -0.00000100  
Ca -1.91317500 2.35536600 0.00002500

**Model II**

**PBE**

U 0.00000100 0.44765700 0.00000100  
O -0.00000600 0.42141700 -1.89346600  
O 0.00000200 0.42138500 1.89346700  
O -2.31901000 -0.00400900 0.00000900  
O 0.73333200 2.59985500 -0.00000800  
O -1.58793600 -1.30908300 -0.00000500  
O 1.58794100 -1.30907800 -0.00000600  
O 2.31901200 -0.00400300 0.00000400  
O -0.73336600 2.59984000 0.00001000  
Ca 3.86003400 -1.71287200 -0.00000300  
Ca -3.86002600 -1.71288200 -0.00000400

**PBE0**

U 0.00000000 0.44511100 0.00000000  
O 0.00007300 0.41989200 -1.84032900

O -0.00007400 0.41990200 1.84032800  
 O -2.29330800 -0.00920400 -0.00004500  
 O 0.72351700 2.57822100 0.00005300  
 O -1.57638400 -1.28827200 -0.00002200  
 O 1.57638200 -1.28827200 0.00002200  
 O 2.29330700 -0.00920500 0.00004900  
 O -0.72351600 2.57822100 -0.00005700  
 Ca 3.84084100 -1.70401200 -0.00000400  
 Ca -3.84084100 -1.70401200 0.00000600

#### **M06-L**

U 0.00000000 0.45377800 -0.00000500  
 O 0.00002300 0.42764700 -1.86899600  
 O -0.00002100 0.42762600 1.86898500  
 O -2.33190100 -0.01488400 0.00000600  
 O 0.73071900 2.62460400 0.00003100  
 O -1.59829700 -1.31193200 -0.00000200  
 O 1.59829900 -1.31193600 0.00000700  
 O 2.33189900 -0.01488500 0.00001700  
 O -0.73072600 2.62460100 0.00000000  
 Ca 3.86935300 -1.73385600 0.00000200  
 Ca -3.86934900 -1.73386100 0.00000000

#### **B3LYP**

U 0.00000100 0.45176500 0.00000200  
 O 0.00004500 0.42548100 -1.86441900  
 O -0.00004500 0.42546100 1.86442200  
 O -2.32149100 -0.01037100 -0.00003700  
 O 0.73540800 2.60942500 0.00002800  
 O -1.58876700 -1.30982900 -0.00002700  
 O 1.58877100 -1.30982500 0.00001600

O	2.32149300	-0.01036400	0.00003300
O	-0.73543700	2.60941200	-0.00003100
Ca	3.86880600	-1.72493300	-0.00000700
Ca	-3.86880100	-1.72494000	0.00000400

### **Model III**

#### **PBE**

U	-0.58186200	-0.08296000	-0.09423500
O	-2.07558200	-0.29351600	-1.23598100
O	1.06875900	0.15081300	0.97635400
O	-1.85716300	0.55283600	1.65004000
O	0.40110400	1.56868600	-1.43584800
O	-1.69747800	-0.89989700	1.68360000
O	0.15278000	-2.29442700	-0.29122100
O	0.76537500	-1.50159800	-1.38631900
O	-0.44113000	2.23080900	-0.40972900
Ca	1.78789600	2.35061200	0.30442000
Ca	2.36200300	-1.77447700	0.30870200

#### **PBE0**

U	-0.01819700	-0.57290200	-0.09610400
O	-0.05962400	-2.03534000	-1.21087000
O	0.01983700	1.03032400	0.94179000
O	-0.80086500	-1.74770200	1.63429200
O	-1.50835900	0.63710300	-1.40104000
O	0.64175700	-1.79660200	1.65272400
O	2.25663100	-0.23469700	-0.33214800
O	1.57724600	0.51584100	-1.37783400
O	-2.25836100	-0.08085400	-0.38010100
Ca	-2.07877800	2.12680300	0.31748200
Ca	2.21517900	1.99332000	0.31386900

**M06-L**

U	-0.58479100	-0.08700200	-0.09976100
O	-2.04541700	-0.30038300	-1.24306000
O	1.02911600	0.14908900	0.96965300
O	-1.89370600	0.53466900	1.64494900
O	0.41213800	1.59232300	-1.42526400
O	-1.72526800	-0.90997000	1.67898800
O	0.18088000	-2.30392600	-0.30428300
O	0.79979100	-1.50175900	-1.38072700
O	-0.43765100	2.24616100	-0.40881300
Ca	1.78345000	2.36577000	0.31937100
Ca	2.37863800	-1.76804500	0.32695300

**B3LYP**

U	0.02791300	-0.57723500	-0.09626500
O	0.08570900	-2.06304300	-1.21929900
O	-0.02352000	1.05496800	0.94915900
O	-0.64086500	-1.80857300	1.67684700
O	-1.59789100	0.50215400	-1.40263600
O	0.82486000	-1.75397800	1.65997400
O	2.29304000	-0.05595400	-0.38332700
O	1.52176000	0.65651800	-1.42725100
O	-2.28103600	-0.27242000	-0.34239400
Ca	-2.26590700	1.98065400	0.31436000
Ca	2.06468400	2.17076000	0.32402800

**Model IV****PBE**

U	-0.00000100	-0.39688700	0.00000500
O	-1.25594700	-0.27926100	-1.47711700

O 1.25593800 -0.27925000 1.47713300  
O -1.88845500 -0.37404200 1.32400000  
O 0.58882400 1.80488300 -0.43636300  
O -1.51711200 -1.75965700 1.04099400  
O 1.51707700 -1.75967500 -1.04100800  
O 1.88844300 -0.37406400 -1.32400400  
O -0.58878400 1.80489500 0.43636600  
Ca -2.85592400 1.15608200 -0.34754900  
Ca 2.85593400 1.15606700 0.34752700

#### PBE0

U -0.00000300 -0.43870100 0.00000200  
O -0.80222500 -0.41884300 -1.66568700  
O 0.80222900 -0.41884100 1.66568800  
O -2.08921800 -0.49348000 0.97209600  
O 0.62330800 1.77566200 -0.35943400  
O -1.67829600 -1.84650800 0.68275900  
O 1.67830700 -1.84648600 -0.68278600  
O 2.08921000 -0.49344900 -0.97210400  
O -0.62329600 1.77567900 0.35942700  
Ca -2.92139400 1.40227500 -0.28268400  
Ca 2.92139900 1.40225800 0.28268900

#### M06-L

U 0.00000200 -0.42078100 0.00000500  
O -1.20186400 -0.30301700 -1.47783700  
O 1.20187900 -0.30303900 1.47783700  
O -1.93753300 -0.34036200 1.28261700  
O 0.59651100 1.80659600 -0.41952800  
O -1.59913700 -1.73315100 1.03742100  
O 1.59911100 -1.73315200 -1.03745500

O 1.93753300 -0.34036000 -1.28262000  
O -0.59650400 1.80659300 0.41956500  
Ca -2.84536400 1.19577300 -0.36807800  
Ca 2.84535400 1.19577500 0.36805400

### B3LYP

U 0.00000300 -0.43999000 -0.00000100  
O -0.82182900 -0.41675900 -1.68438200  
O 0.82182600 -0.41673300 1.68438300  
O -2.10891100 -0.51736100 0.99141400  
O 0.63416600 1.80526300 -0.36589900  
O -1.67513000 -1.88710100 0.68581600  
O 1.67508200 -1.88717000 -0.68576700  
O 2.10891600 -0.51745200 -0.99138700  
O -0.63413600 1.80526900 0.36585600  
Ca -2.94413300 1.41837200 -0.28359200  
Ca 2.94412500 1.41839800 0.28358500

### Model V

#### PBE

U -0.00000100 0.26125100 -0.00000100  
O -1.37219200 0.16550500 -1.36362400  
O 1.37220000 0.16552600 1.36361600  
O -1.75595100 -0.19984500 1.46046400  
O 0.51637600 2.38836200 -0.51670800  
O -1.22967200 -1.48832700 0.94873400  
O 1.22968800 -1.48833100 -0.94872300  
O 1.75594600 -0.19984700 -1.46047100  
O -0.51637600 2.38836200 0.51670600  
Ca 3.17572600 -0.94715900 0.26788400  
Ca -3.17572900 -0.94715800 -0.26787900

**PBE0**

U	0.00000100	0.26820300	0.00000600
O	-1.31783200	0.19326100	-1.33270500
O	1.31782900	0.19321100	1.33271900
O	-1.74931900	-0.20694100	1.43430200
O	0.51524200	2.37885300	-0.50425200
O	-1.21546700	-1.46397200	0.93283900
O	1.21552100	-1.46386400	-0.93295400
O	1.74935700	-0.20678600	-1.43430900
O	-0.51531300	2.37882000	0.50433300
Ca	3.15756500	-0.97739000	0.27192100
Ca	-3.15757600	-0.97737400	-0.27193500

**M06-L**

U	-0.00000100	0.27368900	-0.00000400
O	-1.35303300	0.18438100	-1.34146800
O	1.35303200	0.18440400	1.34146000
O	-1.77824100	-0.21908200	1.45443800
O	0.51339300	2.41995300	-0.51472600
O	-1.23788800	-1.49471300	0.94289600
O	1.23788400	-1.49472800	-0.94288100
O	1.77824500	-0.21910300	-1.45443500
O	-0.51336500	2.41995800	0.51472800
Ca	3.18091300	-0.98570200	0.27700200
Ca	-3.18092100	-0.98569400	-0.27698600

**B3LYP**

U	0.00000200	0.27266700	0.00000100
O	-1.34280300	0.18920800	-1.34439200
O	1.34279800	0.18917800	1.34440100

O -1.76572500 -0.20638700 1.45784600  
 O 0.52034600 2.40585700 -0.51548500  
 O -1.22693300 -1.48482000 0.94357300  
 O 1.22685900 -1.48491500 -0.94350300  
 O 1.76569500 -0.20652200 -1.45783000  
 O -0.52027800 2.40589700 0.51540200  
 Ca 3.18459100 -0.98862400 0.27565700  
 Ca -3.18458500 -0.98864300 -0.27566700

#### **Model VI**

##### **PBE**

U -0.03199100 -0.46368400 -0.00004500  
 O -0.28645900 1.46123400 -0.14831200  
 O 0.08990000 -2.34948300 0.13561200  
 O -2.25110200 -0.41594100 0.77225000  
 O 1.71420000 -0.11695000 1.45766200  
 O -2.27797700 -0.52084700 -0.71169300  
 O 0.70524600 -0.43376600 -2.18269500  
 O 1.86735100 -0.30685100 -1.29883800  
 O 0.46191400 -0.12663900 2.21802800  
 Ca -2.66764600 1.70777700 -0.08634700  
 Ca 2.80557700 1.54886600 -0.01025100

##### **PBE0**

U -0.03131000 -0.43357800 0.00901700  
 O -0.31964200 1.40923600 -0.21322600  
 O 0.14323500 -2.25359800 0.21671100  
 O -2.22309600 -0.43185600 0.78549500  
 O 1.67587900 0.00639600 1.45366100  
 O -2.26291400 -0.59460100 -0.66405600  
 O 0.70144800 -0.48683000 -2.15807100

O	1.84148100	-0.30542600	-1.29388000
O	0.44199000	-0.00207600	2.19460200
Ca	-2.74931600	1.62448200	-0.13237600
Ca	2.89399100	1.43348000	-0.03759600

### M06-L

U	-0.03153800	-0.46549800	-0.00101500
O	-0.29036900	1.42649900	-0.15344800
O	0.10184700	-2.32501600	0.13919800
O	-2.26683300	-0.41248800	0.78026400
O	1.71944000	-0.09927400	1.46649400
O	-2.30158300	-0.52532500	-0.69698400
O	0.73710400	-0.43413100	-2.19287700
O	1.88424000	-0.29874900	-1.29922800
O	0.47570800	-0.11588400	2.23041500
Ca	-2.69759400	1.70340600	-0.09617300
Ca	2.81884600	1.55163300	-0.00869400

### B3LYP

U	-0.02868700	-0.45976000	0.00334300
O	-0.28516200	1.42936600	-0.07380100
O	0.10268700	-2.31839500	0.06851000
O	-2.26901100	-0.45829900	0.73628900
O	1.74503800	-0.14662500	1.44362300
O	-2.26766200	-0.50385300	-0.74788200
O	0.65574900	-0.35514500	-2.20260300
O	1.83892600	-0.25341200	-1.34153800
O	0.50762100	-0.18678100	2.23053200
Ca	-2.71632500	1.69721600	-0.04593000
Ca	2.83701000	1.53493900	-0.01470200

### Ca<sub>2</sub>[Np(V)O<sub>2</sub>(O<sub>2</sub>)<sub>3</sub>] Geometries

**Model I****PBE**

Np	0.53864700	0.00000000	0.00000400
O	0.35082000	2.00950000	0.00008300
O	0.35081900	-2.00950000	-0.00008000
O	-1.84089800	-0.00005500	0.75208800
O	2.27209800	-0.00003800	1.53801200
O	-1.84089600	0.00005600	-0.75211700
O	0.98087600	0.00003700	-2.29047100
O	2.27210000	0.00004100	-1.53800400
O	0.98087300	-0.00004300	2.29047900
Ca	-1.95751200	-2.24893000	-0.00011100
Ca	-1.95751200	2.24893100	0.00009800

**PBEO**

Np	0.55098900	-0.00000600	0.00000400
O	0.33746800	1.96457700	0.00006900
O	0.33744400	-1.96458500	-0.00006600
O	-1.83779100	-0.00005300	0.73810000
O	2.26798000	-0.00001900	1.52964700
O	-1.83778100	0.00007800	-0.73813400
O	0.99507700	0.00002600	-2.25002200
O	2.26798300	0.00003800	-1.52963900
O	0.99507500	-0.00005100	2.25003000
Ca	-1.98615400	-2.22648500	-0.00012600
Ca	-1.98612800	2.22650900	0.00011100

**M06-L**

Np	0.54559200	0.00000000	0.00000800
O	0.36335900	1.98949700	0.00008500
O	0.36335900	-1.98949700	-0.00008000

O -1.84465300 -0.00004400 0.75014600  
O 2.28061100 -0.00004000 1.56863200  
O -1.84464400 0.00004400 -0.75019100  
O 0.98810400 0.00004700 -2.31233200  
O 2.28060300 0.00004100 -1.56862900  
O 0.98811500 -0.00004900 2.31234300  
Ca -1.98347300 -2.24349200 -0.00011300  
Ca -1.98347300 2.24349200 0.00008800

### B3LYP

Np 0.57134000 -0.01147100 -0.00207300  
O 0.36776000 1.97682200 -0.01704900  
O 0.30497200 -1.98834800 -0.02851500  
O -1.83447100 0.02603300 0.75801200  
O 2.26321800 0.01043300 1.58098700  
O -2.06697900 0.02619400 -0.73100200  
O 1.06999400 -0.02542200 -2.27116600  
O 2.35201100 0.01904700 -1.51070500  
O 0.95924300 -0.04489800 2.29772100  
Ca -2.04096600 -2.19974700 -0.01400700  
Ca -1.98206500 2.25314200 -0.00766600

### Model II

#### PBE

Np -0.00000100 0.27875000 0.00000000  
O -1.42822100 0.16803400 -1.39899200  
O 1.42822200 0.16804700 1.39899000  
O -1.84081300 -0.24843200 1.48972400  
O 0.57705000 2.47448800 -0.47033200  
O -1.26511700 -1.54164000 0.98739200  
O 1.26511700 -1.54166000 -0.98737200

O 1.84080900 -0.24846100 -1.48972800  
O -0.57703900 2.47449800 0.47031000  
Ca 3.11454200 -0.98906600 0.29086700  
Ca -3.11454200 -0.98907100 -0.29086500

#### PBE0

Np 0.00000800 0.25534600 -0.00000900  
O -1.36455200 0.12803700 -1.39192200  
O 1.36452300 0.12795800 1.39194600  
O -1.83343000 -0.17037500 1.43110200  
O 0.52763500 2.45565300 -0.51163500  
O -1.31659800 -1.48276900 1.02067300  
O 1.31668900 -1.48245800 -1.02097500  
O 1.83358700 -0.16999300 -1.43105700  
O -0.52785500 2.45541900 0.51194500  
Ca 3.12969500 -0.96600800 0.29891000  
Ca -3.12973300 -0.96593900 -0.29889700

#### M06-L

Np -0.00000100 0.28002400 -0.00001400  
O -1.40876400 0.19380000 -1.37551800  
O 1.40876200 0.19391500 1.37548600  
O -1.85784200 -0.28204900 1.48439700  
O 0.57605400 2.51142700 -0.47555400  
O -1.29206200 -1.57040300 0.96273600  
O 1.29207400 -1.57044500 -0.96268500  
O 1.85786200 -0.28210200 -1.48436400  
O -0.57606300 2.51140500 0.47554900  
Ca 3.14814000 -0.99216400 0.29706700  
Ca -3.14814300 -0.99216600 -0.29702000

#### B3LYP

Np	0.00000500	0.22355800	0.00001500
O	-1.34846800	0.12238200	-1.43999000
O	1.34845900	0.12228700	1.44002200
O	-1.87659800	-0.15397500	1.45000100
O	0.54515500	2.44816800	-0.51234700
O	-1.44970700	-1.53289300	1.04973800
O	1.44981000	-1.53255800	-1.05006200
O	1.87671100	-0.15356200	-1.44998400
O	-0.54536800	2.44803000	0.51257900
Ca	3.20554700	-0.87338400	0.32202400
Ca	-3.20556700	-0.87331300	-0.32207500

### Model III

#### PBE

Np	-0.11917200	-0.57150100	-0.10236200
O	-0.48565900	-2.07731600	-1.26965000
O	0.26704700	1.140444000	0.99645300
O	-1.15287300	-1.61029400	1.69242300
O	-1.43763400	0.97229700	-1.43193000
O	0.30562600	-1.87792100	1.76236200
O	2.30566700	-0.62372700	-0.37803600
O	1.74214300	0.28277200	-1.43813000
O	-2.34779300	0.38534000	-0.38979000
Ca	-1.60369300	2.45522100	0.32233200
Ca	2.47923300	1.56562200	0.33617200

#### M06-L

Np	-0.12213200	-0.56620700	-0.11525400
O	-0.51920300	-2.06741600	-1.23791600

O	0.27814000	1.10540500	0.96797000
O	-1.18062800	-1.62133200	1.71050400
O	-1.46363200	1.00129100	-1.42861800
O	0.28279100	-1.89680500	1.77675300
O	2.31699800	-0.63747500	-0.39199200
O	1.77835600	0.30109500	-1.43587700
O	-2.36159700	0.39480300	-0.39076600
Ca	-1.61512800	2.46378600	0.34630000
Ca	2.53055100	1.53725200	0.36160700

#### B3LYP

Np	-0.11912300	-0.57202800	-0.10925900
O	-0.49572800	-2.06335200	-1.25061300
O	0.26911100	1.09652000	0.99704900
O	-1.14924100	-1.62465800	1.70798800
O	-1.46439300	0.98430100	-1.43174600
O	0.31250600	-1.90986400	1.75442400
O	2.31636900	-0.61755200	-0.40213900
O	1.77726700	0.31353900	-1.44916800
O	-2.36621800	0.38382500	-0.39624400
Ca	-1.62220800	2.46086300	0.33965000
Ca	2.49626200	1.57396300	0.35658400

#### Model IV

#### PBE

Np	0.00000100	0.38720900	-0.00000200
O	1.30604800	0.26226200	-1.51102100
O	-1.30605900	0.26233300	1.51101300
O	2.03731800	0.39116100	1.29212900
O	-0.62507100	-1.89385400	-0.40141900
O	1.48998100	1.76953200	1.18482200

O	-1.48998600	1.76943100	-1.18492400
O	-2.03728200	0.39103500	-1.29217200
O	0.62511600	-1.89384300	0.40145900
Ca	2.82133900	-1.11189600	-0.37928100
Ca	-2.82136800	-1.11185100	0.37933500

#### PBE0

Np	0.00000000	0.36973600	-0.00000600
O	1.23519800	0.25735200	-1.48941700
O	-1.23517900	0.25732800	1.48941800
O	2.02742700	0.43961500	1.23560200
O	-0.62553400	-1.88394600	-0.37438100
O	1.51097800	1.80230100	1.11491700
O	-1.51101600	1.80230700	-1.11488300
O	-2.02745900	0.43961900	-1.23557100
O	0.62554900	-1.88394700	0.37435000
Ca	2.82557200	-1.10575300	-0.36581800
Ca	-2.82555900	-1.10577100	0.36583300

#### M06-L

Np	0.00611000	0.45864500	0.00788300
O	1.17966500	0.26772800	-1.54689400
O	-1.19003400	0.35163600	1.55244000
O	2.11721800	0.35853500	1.25449100
O	-0.60501800	-1.90917600	-0.36002300
O	1.84958800	1.77322400	0.87234900
O	-1.80540400	1.72504700	-0.98082000
O	-2.02310300	0.28961600	-1.31053500
O	0.59409300	-1.88671800	0.52074100
Ca	2.72441400	-1.29940300	-0.42060300
Ca	-2.79962700	-1.22125200	0.38324700

**B3LYP**

Np	0.00000000	0.36947900	-0.00000400
O	1.25022300	0.25889100	-1.51421100
O	-1.25020800	0.25889700	1.51420400
O	2.05224100	0.43364700	1.28860800
O	-0.62179500	-1.93753600	-0.40895800
O	1.60276000	1.82584000	1.01473800
O	-1.60280300	1.82582400	-1.01472500
O	-2.05231700	0.43363800	-1.28858100
O	0.62186400	-1.93747700	0.40900100
Ca	2.90809600	-1.09137000	-0.36205500
Ca	-2.90808100	-1.09139900	0.36204400

**Model V****PBE**

Np	0.00000000	0.26085600	-0.00000900
O	-1.40976300	0.16992900	-1.41088100
O	1.40978600	0.17005000	1.41085500
O	-1.83401000	-0.24056000	1.49930300
O	0.51046800	2.46857300	-0.54543200
O	-1.28539800	-1.53990500	0.98939900
O	1.28542300	-1.53994500	-0.98934200
O	1.83402000	-0.24061700	-1.49930500
O	-0.51052500	2.46855700	0.54539900
Ca	3.12603900	-0.94969600	0.29572100
Ca	-3.12603800	-0.94971700	-0.29567800

**PBE0**

Np	-0.00000300	0.25534800	-0.00000400
O	1.36459000	0.12809300	1.39188600

O	-1.36456500	0.12799400	-1.39191100
O	1.83345100	-0.17032700	-1.43108700
O	-0.52764200	2.45560700	0.51168300
O	1.31658400	-1.48272400	-1.02073000
O	-1.31668700	-1.48248100	1.02095100
O	-1.83356200	-0.17001700	1.43108300
O	0.52785000	2.45547400	-0.51189200
Ca	-3.12968800	-0.96601800	-0.29889500
Ca	3.12969400	-0.96599800	0.29891900

#### M06-L

Np	0.00000100	0.26203300	0.00000900
O	1.38803100	0.18226100	1.40419100
O	-1.38802800	0.18233200	-1.40417600
O	1.84581200	-0.26679200	-1.50011700
O	-0.53331600	2.49601600	0.52102200
O	1.29934400	-1.55750100	-0.97717100
O	-1.29936800	-1.55751600	0.97715100
O	-1.84583100	-0.26680900	1.50011200
O	0.53334400	2.49599800	-0.52102800
Ca	-3.15043400	-0.95082000	-0.30060600
Ca	3.15043400	-0.95082800	0.30056900

#### B3LYP

Np	-0.00000700	0.22357400	-0.00001700
O	1.34850600	0.12244700	1.43996600
O	-1.34847900	0.12217900	-1.44000900
O	1.87655900	-0.15409000	-1.45000500
O	-0.54510000	2.44824900	0.51223100
O	1.44960600	-1.53298400	-1.04969500
O	-1.44976800	-1.53244800	1.05017900

O	-1.87672000	-0.15344300	1.44999500
O	0.54543700	2.44796200	-0.51268800
Ca	-3.20553600	-0.87343000	-0.32200000
Ca	3.20555100	-0.87333800	0.32209000

### **Model VI**

#### **PBE**

Np	0.01839000	-0.54387300	-0.00261300
O	-0.11209100	1.51938900	-0.13563900
O	0.14863000	-2.46877200	0.17527500
O	-2.31425500	-0.44595200	0.67654900
O	1.70794700	0.04573500	1.57683400
O	-2.28291500	-0.42256500	-0.82661600
O	0.84352500	-0.49221800	-2.21824800
O	1.97299600	-0.18235600	-1.29662300
O	0.42423100	-0.19932700	2.28884700
Ca	-2.45509100	1.74936200	-0.07437000
Ca	2.21434900	1.83807200	-0.00963100

#### **PBE0**

Np	0.01427800	-0.54327000	-0.00028200
O	-0.11643300	1.44836500	-0.15330800
O	0.15077400	-2.42130500	0.18760900
O	-2.30267500	-0.45271500	0.65188700
O	1.68611000	0.05031900	1.54183000
O	-2.23634400	-0.40971800	-0.81723700
O	0.84114800	-0.46245200	-2.20994300
O	1.93952400	-0.17334000	-1.28808100
O	0.44413400	-0.15132000	2.28580400
Ca	-2.45170500	1.74417700	-0.06877300
Ca	2.22281900	1.81089400	-0.00933900

**M06-L**

Np	0.01048100	-0.54913500	-0.00121700
O	-0.10214000	1.46943000	-0.18762700
O	0.11560300	-2.44958000	0.21509700
O	-2.33779800	-0.41733600	0.68113000
O	1.71447600	0.06279200	1.58318600
O	-2.30850500	-0.41672900	-0.82097200
O	0.89807400	-0.52209200	-2.23139300
O	2.00230600	-0.20042500	-1.28231000
O	0.43595700	-0.13444300	2.32287600
Ca	-2.47157400	1.76842200	-0.09285900
Ca	2.25564700	1.82841000	-0.01347800

**B3LYP**

Np	0.01221000	-0.54462000	-0.00171600
O	-0.10014800	1.47994900	-0.16405600
O	0.11752600	-2.44492900	0.19090600
O	-2.33401500	-0.44103200	0.66629600
O	1.72152500	0.04265900	1.60134100
O	-2.30450300	-0.41137000	-0.83284100
O	0.86608800	-0.49943600	-2.23757900
O	1.98527500	-0.19874900	-1.30067700
O	0.43285900	-0.17159600	2.31942600
Ca	-2.47481100	1.76908900	-0.07269500
Ca	2.26419200	1.82119600	-0.01645100